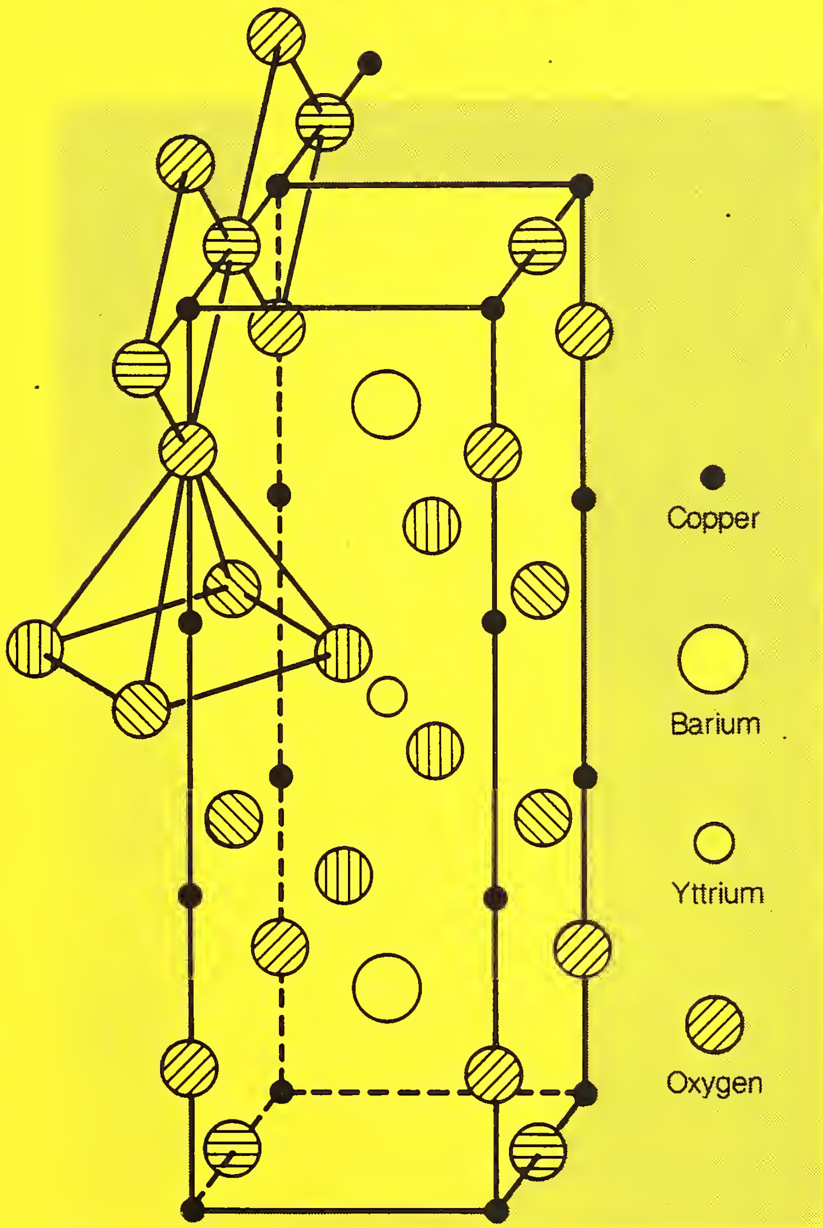
IMSE

Institute for Materials Science and Engineering

CERAMICS



NAS-NRC
Assessment Panel
January 21-22, 1988

NBSIR 87-3612
U.S. Department of Commerce
National Bureau of Standards

Technical Activities 1987

The crystal structure illustrated is that of $Ba_2YCu_3O_7$, a superconducting oxide with a transition temperature of 90-95K. Crystallographic analysis performed at the NBS was the first determination of the structure of this important compound which clearly identified the structure as orthorhombic and specified the lattice sites of the oxygen atoms.

IMSE

Institute for Materials Science and Engineering

CERAMICS

NAS-NRC
Assessment Panel
January 21-22, 1988

NBSIR 87-3612
U.S. Department of Commerce
National Bureau of Standards

Technical Activities 1987

TABLE OF CONTENTS

INTRODUCTION

Introduction

Ceramic materials are becoming increasingly important in our technological society in a variety of sophisticated electronic, optical, and mechanical applications and the intense international competition in this field has demonstrated the value of close industrial, academic and governmental interactions. With this environment, the Ceramics Division has set as its objective, the development of basic understanding, novel measurement methods, standard reference materials, and standard reference data to enable industry to achieve key properties of ceramic materials through advanced processing.

In the past year, the Division has aggressively addressed this goal and taken measures to strengthen its capabilities through staff expansion, acquisition of sophisticated equipment and the construction and remodeling of existing facilities. This was exemplified by the completion of the Division's "Level 10 Clean Room," which will allow processing of ceramics under rigorously controlled conditions. We have also initiated the design and construction of a surface forces laboratory which will allow the measurement of phenomena critical to our understanding of fracture, sintering, and tribology.

In 1987, the Division was active in the newly emerging field of high temperature superconductors through development of basic data required for processing, as well as the measurement of physical properties of this unique class of materials.

The Division staff has been productive in several fields of Ceramic Research: 1) approximately 200 papers and reports were published; and, 2) 160 invited talks presented. The skill and expertise of the Division were recognized by the appointment of Dr. Brian Lawn, a member of the Mechanical Properties Group, as an NBS fellow and Dr. Edwin Fuller, leader of the Processing Science Group, was awarded the Ross Purdy Coffin Award by the American Ceramic Society.

Among the significant accomplishments by the Division in 1987 are:

- The phase diagram for the superconducting YBaCuO system was determined and published.
- A diamond film deposition apparatus was constructed and successful deposition of diamond films demonstrated.
- A theoretical model of the role of surface forces in subcritical crack growth was developed.
- A time-resolved micro-Raman test system to analyze reactions at tribological contacts was developed.
- The interrelationships between processing, microstructure, and properties of superconducting YBaCuO were determined.

- A novel technique for measurement of sintering stress in ceramics was invented.

- Low temperature "sintering" through the application of high pressure was demonstrated, with the potential for enhanced toughness through pressure induced phase transformations.

- As part of the International Energy Agency (IEA) international powder characterization round-robin, 2000 silicon nitride reference powder samples were prepared, certified and distributed.

- Standard Reference Material 6406, silicon powder, was certified for calibration of x-ray line positions in x-ray powder diffraction.

- Techniques to predict the effect of filaments on crack growth retardation in ceramic matrix components were developed.

- The first data on the fracture behavior of superconducting ceramics as a function of sintering and annealing conditions were obtained.

- Volume 6 of Phase Diagrams for Ceramics was completed.

During the past year many national and international visitors from industry and academia have come to the Division for information exchanges. Our ties with domestic industry have been strengthened by these visits as well as through collaborative research efforts. Similar relationships with the university community have also been strengthened through the Divisions efforts to augment staff with university postdoctoral and graduate students.

In 1988, the Bioprocessing activity will be transferred to the Polymers Division and the High Temperature Chemistry activity to the Metallurgy Division to more effectively integrate the research of those groups into the IMSE program. Concurrently, the Wear Group will be transferred from the Metallurgy Division to Ceramics, again to facilitate research integration.

We look forward to the increased emphasis on industrial cooperation, which the establishment of the National Institute of Standards and Technology will entail, and anticipate much greater participation with the private sector on research of mutual interest.

S. M. Hsu
Chief, Ceramics Division

September 1987

TECHNICAL ACTIVITIES

PROCESSING

CERAMIC POWDER CHARACTERIZATION

Alan Dragoo

The work of the Powder Characterization Group is focussed on measurements of physical and phase characteristics of powders and on understanding the effect of powder characteristics on processes of dispersion, consolidation and sintering which convert powders into ceramics. Processing of ceramic materials typically begins with a powder which is manipulated through several processing steps and consolidated and sintered into a hard, solid object. Characterization and control of properties of the starting powder is recognized as essential to the production of high-quality ceramics required in advanced technological applications, such as electronic substrates, cutting tools and engine components.

The connection between powder characteristics and processing and performance begins with the recognition that powders are complex physical systems in which characteristics are often spatially distributed within particles, between particle interior and surface, and between particles. Powders, dispersions and ceramics are generally described by properties that are based on these variable particulate ensembles. There is a critical need for Standard Reference Materials (SRM's) with certified particle size distributions to be used in the calibration and intercomparison of instruments for particle size measurements.

The Powder Characterization Group recognizes that the development of rapid, on-line sensors for particle characteristics is an round-robin on powder characterization, the JCPDS-International Centre for Diffraction Data, the American Ceramic Society and visits to companies. Work of the group is carried out primarily in two laboratories: the Fine Powder Laboratory and the Automated X-Ray Diffraction Laboratory. Development of Scanning Electron Microscopy/Image Analysis Laboratory for direct characterization of particles and microstructures was begun with the initiation of the purchase of a scanning electron microscope/image analysis (SEM/IA) system.

Representative Accomplishments

- A numerical descriptor was developed for description of the fiber distribution in fiber-reinforced composites.

- Over 2000 silicon nitride reference powder samples were prepared and certified for a international powder characterization round-robin.

- Standard Reference Material 640b, silicon powder, was certified as new reference material for calibration of x-ray line positions in x-ray powder diffraction.

Powder Characterization

A. Dragoo, C. Robbins, J. Kelly, D. Minor

Research is carried out with a variety of instruments, including an x-ray gravitational sedigraph, photon correlation (quasi-elastic light scattering) spectrometer, Brunauer-Emmett-Teller (BET) surface area

apparatus, mercury intrusion porosimeter and automatic helium pycnometer. Powders are characterized for research in ceramic processing, for preparation of Standard Reference Materials, for studies of wear of ceramic components and for development of new measurement methods. Preparation of samples of five ceramic powders for an international round-robin conducted on the auspices of the International Energy Agency has constituted a major effort during the last year. Approximately, 1000 zirconia and 3500 silicon nitride powder samples have been prepared to date. The assurance of physical and chemical homogeneity between samples is critical to the success of the round-robin. A major effort in the statistical analysis of the results of the round-robin was recently initiated.

Electron Microscopy/Image Analysis

J. Kelly, D. Minor, A. Dragoo

Direct characterization of particles can provide fundamental size and shape data that not only serves to verify indirect measurements but provides data which is not accessible by indirect means. For ultrafine particles scanning electron microscopy (SEM) and transmission electron microscopy (TEM) must be used to obtain high-resolution images. However, to achieve measurements with standard errors of a few percent, on the order of 10,000 images must be measured. Consequently, automated image analysis (IA) is required. Purchase of an integrated SEM and IA systems was initiated this year. This will be an unique Institute facility.

The Powder Characterization Group has been assisting the Army Materials Technology Laboratory in the development of quantitative image analysis procedures for evaluation of composite materials. Initial work on graphite fiber reinforced polymer material has led to the development of a quantitative descriptor for variation in fiber distribution. This descriptor can be compared with computer generated simulated random dispersions. Establishment of such a descriptor is viewed as the first step toward the development of quantitative description of ceramic composite microstructures. The ultimate goals of this work are: 1) to develop Standard Reference Materials for two phase dispersions and 2) to obtain numeric image descriptors of composites which correlate with their mechanic properties.

An SEM study was conducted in collaboration with the Optical Materials Group on thin diamond films formed by electron assisted chemical vapor deposition using 99.5 percent H_2 and 0.5 percent CH_4 at 40 Torr pressure. High-quality micrographs showed the development of individual diamond crystals which evidenced multiple twinning. The deposition process was followed from individual crystals to the development of a continuous film.

Application of X-ray Diffraction to Ceramic Processing

J. Cline

Research in the field of x-ray diffraction is centered around the broadening of its application to the characterization of ceramic materials before, during and after processing. The aim is to assist the development of process characterization and modeling that is applicable to a broad

range of ceramic systems. Investigation of the application of XRD to quantitative analysis has lead to the isolation of microabsorption and extinction effects. With the use of a high-temperature x-ray diffractometer these effects can be used to measure grain growth during sintering. High-temperature studies are planned to measure grain growth and orientation effects in thin films of superconducting oxide materials.

<u>Standard Reference Materials For X-Ray Diffraction</u>

C. Robbins, C. Hubbard, J. Cline, A. Dragoo, M. Kuchinski[1], Y. Zhang[2], W. Wong-Ng[2], J. Stewart[2], T. Nakamura[3], L. Domingues[4]

[1]Guest Scientist, Rutgers University
[2]Guest Scientist, University of Maryland
[3]Guest Scientist, Meiji University, Japan
[4]Guest Scientist, Trans Tech, Adamstown, MD

Work on SRM's has focused on the certification of SRM 640b to replace SRM 640a, which is now depleted, and on the certification of a new quantitative SRM for respirable cristobalite (SRM 1879). A synthesis method for the preparation of alkali-stabilized tridymite has been scaled up to produced material in quantity for a respirable tridymite SRM. Several silicon nitride powders, including a beta-silicon nitride powder, for investigation of alpha/beta phase ratios in bulk and surface compositions. The silicon nitride study is using both x-ray diffraction and Fourier transform infrared spectroscopy. Research is being carried out in collaboration with the University of Maryland to develop a method for certification of an ultrafine crystallite size standard by x-ray line broadening (XRLB). During the past year a magnesium oxide material was found which shows considerable promise as an SRM for this application.

<u>X-Ray Diffraction Reference Patterns</u>

W. Wong-Ng[1], H. McMurdie[2], B. Paretzkin[2], C. Hubbard, A. Dragoo

[1]Guest Scientist, University of Maryland
[2]Guest Scientist, JCPDS, Swarthmore, PA

Expansion of the market for new ceramic materials and the increased use of computer automation in x-ray diffraction combine to accentuate the needs for improved reference data in the Powder Diffraction File (PDF) and for additional data for new phases. As an integral part of a continuous effort of NBS to develop measurement methods and data to further the manufacture and use of ceramic materials, NBS is carrying out a program, which is supported by the JCPDS-International Centre for Diffraction Data, to high-quality x-ray diffraction patterns and data for new phases of advanced ceramic materials. These materials include oxides of importance as electronic materials and borides, carbides, nitrides, silicides, selenides and tellurides which are important for engine components and cutting tools due to their high strength or hardness. A total of 65 experimental and 35 calculated patterns were produced and submitted for publication by the JCPDS-ICDD. These patterns included high Tc superconductor and related phases in the BaO-Y_2O_3-CuO system. Phases characterized included $Ba_2YCu_3O_7$, Ba_2YCuO_5, $Ba_2YCu_3O_{6.8}$, $Ba2YCu_3O_6$, $BaCuO_2$, Ba_2CuO_3, $Ba_{Y2}CuO_5$,

$Ba_3Y_4O_9$, $BaSm_2CuO_5$, $BaYb_2CuO_5$, and $La_{1.8}Sr_{0.2}CuO_4$. In conjunction with the production of x-ray patterns a study was carried out on the phase transition of $Ba_2YCu_3O_x$ from the orthorhombic to tetragonal form.

AC Impedance Spectroscopy

A. Dragoo, J. Kelly, J. Sung (Student)

The application of AC impedance spectroscopy to the characterization of slurries and of ceramics during processing was initiated this year. Aqueous slurries of zirconia powder were investigated over a concentration range of 0.08 to 0.4 volume percent powder. Using gain-phase measurements a significant decrease in gain was observed at a concentration of about 0.25 percent. Interpretation of this response is in progress.

In collaboration with the Processing Science Group, zirconia compacts were prepared and sintered at various temperatures and firing times. Samples are being characterized by measurements of grain size and by measurement of the complex AC impedance.

PROCESSING SCIENCE

Edwin R. Fuller, Jr.

The program of the Processing Science Group has as its broad objective the development of a science and technology base for ceramic processing, relating processing both to ceramic microstructures, which are developed, and to material properties and performance, which these microstructures determine. The research effort is in three principal areas: (1) sintering science, (2) microstructural properties, and (3) processing-property relations. In the first area, critical factors influencing ceramic sintering, such as, chemical composition and stress, are addressed. In the second area, microstructural and interfacial properties, such as interatomic forces, surface and grain-boundary energies, and defect and impurity concentrations and their formation energies are studied and related to ceramic sintering. In the third area, relations are studied between these microstructural features and resulting properties, such as, toughening behavior for structural ceramics and superconducting behavior for high-T_c ceramic superconductors.

Representative Accomplishments

- Enhanced cognizance of the importance of chemical composition on sintering of advanced ceramics has resulted in the design and construction of an ultra-clean ceramic processing facility for controlling chemical composition and determining its influences on sintering.

- Demonstration of low-temperature "sintering" of advanced ceramics through the application of high pressure, with the potential for enhanced toughness by pressure-induced phase transformations.

- Development of a novel measurement technique for characterizing the "differential sintering stresses" that develop during the sintering of ceramics with second-phase heterogeneities and/or reinforcing fibers.

- First confirmed observation of diffusion induced grain-boundary migration in an oxide ceramic, MgO by diffusion of NiO solute.

- Theoretical formulation using a lattice statics Green's function method for calculating the atomistic structure and energy of grain-boundary interfaces in ionic ceramics.

- A novel fracture mechanics specimen for evaluating the interaction of matrix cracks with reinforcing fibers in ceramic matrix composites, and thereby the interfacial properties developed during processing.

- Elucidation of the interrelations between processing, microstructure, and superconducting properties for new high T_c ceramic superconductors of the type $YBa_2Cu_3O_{7-x}$, including the influence of annealing conditions and sintered density on the superconducting transition, and the influence of milling media on superconducting phase composition.

SINTERING SCIENCE

J.E. Blendell, S. Block, T.W. Coyle, U.V. Deshmukh[1], E.R. Fuller, Jr., C.A. Handwerker[2], C.P. Ostertag[3], G.J. Piermarini, L.C. Stearns, M.D. Vaudin[4], C.A. Harding, and C.A. Shen

[1]Guest Scientist, Drexel University
[2]Metallurgy Division, IMSE
[3]Guest Scientist, University of California, Santa Barbara
[4]Guest Scientist, Cornell University

Chemical Composition: Impurities are known to dominate sintering and microstructure development in ceramics. Quantitative understanding, however, is lacking for the mechanisms, by which impurities and chemical composition, in general, affect sintering. To facilitate studies of these phenomena, an ultra-clean ceramic processing facility with an extrapolated cleanliness of Class 10 has been designed and constructed during the past year. This laboratory permits the production of ceramic powders with controlled impurity levels, thereby permitting the influence of chemical composition on sintering to be elucidated. Impurity concentrations in the powders will be measured and contamination introduced during various processing steps (i.e., synthesis, compaction, calcination and sintering) documented.

Pressure Sintering: Ceramics are usually sintered at high temperatures, occasionally with the assistance of moderate pressures. An interesting alternative for producing ceramics with potentially superior properties is "high-pressure sintering" at low temperature. Such a process can be accomplished by high-pressure compaction of the material, thereby reducing voids, breaking down aggregates, and enhancing interparticle contact, followed by low-temperature "sintering" under high pressure. Processing by this concept of **pressure sintering** has been applied to ZnS, the toughening of which is of interest for infrared windows, and to $YBa_2Cu_3O_7$ ceramic superconductors. Preliminary results on ZnS in a diamond anvil cell are very encouraging. Processing pressures, initially at 8.4 GPa, have progressively been lowered to a combination of cold pressing at 2.2 GPa followed by sintering at only 550 MPa and 500°C for 5 hours. Microindentation tests give a hardness of 3.4 ± .1 GPa and a toughness, Kc, of 1.55 ± .15 $MPa.m^{1/2}$, which is greatly superior to values obtained for both hot-pressed (Kc=0.44) and CVD (Kc=1.0) prepared ZnS. For $YBa_2Cu_3O_7$ superconductors, cold pressing at 4.5 GPa followed by sintering at 1.6 GPa and 500°C for 1 hour gives a hardness of 5.5 ± 1.5 GPa. As no cracks were observed, toughness could not be determined. X-ray diffraction measurements of atomic cell volume versus pressure give a bulk modulus of 196 ± 17 GPa. Extension of pressure sintering to larger samples is being explored with large presses.

Sintering Ceramic Composites: Fiber reinforced ceramics are generally produced by hot-pressing, in order to achieve full density and thereby good properties. The inability to sinter such materials in the absence of pressure derives from the presence of already dense fibers. These fibers cause stresses to develop during sintering, due to the constraints they impose on the contracting matrix. A new method has been developed to reveal, monitor, and measure these stresses during densification of ceramic

composites, by incorporating a layer of SiC fibers between two layers of ceramic powder of different thicknesses. Upon sintering, this configuration produces an asymmetric stress field across the thickness of the specimen, which results in bending of the compact, as characterized by curvature of the fibers. To relieve this stress development, polymer coating of an appropriate thickness have been applied to the fibers. The polymer burns off at the relatively low temperature of 600°C, producing a gap between the matrix and fibers, thereby allowing the matrix to shrink in an unconstrained manner onto the fibers. During sintering no stresses were observed and after sintering the composite reached the same final density as the monolithic material.

MICROSTRUCTURAL PROPERTIES

J.E. Blendell, E.R. Fuller, Jr., C.A. Handwerker, R.F. Krause, Jr., L.C. Stearns, V.K. Tewary[1], M.D. Vaudin, C.A. Harding, and C.A. Shen[2]

[1]Guest Scientist, Ohio State University
[2]Summer Student, Massachusetts Institute of Technology

Interfacial Stability in Ceramics: Of particular importance to the properties and performance of advanced ceramic materials, during both processing steps and in-service use, is the stability of boundaries and interfaces in these materials. Diffusion induced grain-boundary migration (DIGM) is a mechanism, by which otherwise stable boundaries can be induced to migrate, due to the diffusion of a solute into or out of the material. In the past year DIGM has been studied in the MgO/NiO system. Sintered MgO specimens were exposed to NiO at 1100°C to 1300°C for times up to 100 hours, and their microstructures characterized by optical and electron microscopy. Similarities with DIGM in metallic systems were found, with boundaries migrating up to 5 μm. Alloying of the regions in the vicinity of the grain boundaries was observed, together with an increased dislocation density and a change in lattice parameter caused by the change in chemical composition.

IEA Ceramic Characterization: The reproducibility and precision, with which ceramic microstructural properties can be measured, has not been assessed in a systematic manner for advanced ceramic materials. The objective of this work is to measure and characterize ceramic properties (crystalline phase composition, grain-boundary properties and possible surface residual stresses) for a series of standard ceramic specimens to assist in the development of internationally accepted standards for ceramics characterization. The work will contribute to an international round-robin, IEA ANNEX II, Subtask 3 on Ceramics Characterization, under the auspices of the International Energy Agency. To date an ESK silicon carbide material has been examined by transmission electron microscopy. Observations show that the material is mainly α-SiC of the 6H polytype with a 1-3 μm grain size. The microstructure is essentially equiaxed, with a number of grain boundaries lying in the basal plane of one of the adjoining crystals. The grain boundaries are not decorated by any precipitates at a resolution of 2 nm.

Structure and Energy of Ceramic Grain Boundaries: Theoretical studies have been undertaken to elucidate the structure and energy of ceramic grain boundaries, and their dependence on defect and chemical composition. A Green's function method has been developed for these calculations. Using a coincidence-site-lattice as a reference state, the Green's function is obtained in terms of the perfect lattice Green's function by mapping lattice sites of the reference state to the perfect lattice, and then solving the appropriate Dyson's equation. This Green's function gives the response of the reference state to the non-equilibrium forces, thereby determining the atomistic structural relaxations. Both harmonic and anharmonic theories have been developed. For purposes of illustration, the method has been applied to a $\Sigma 5$ tilt boundary in both copper and a simplistic model of MgO. The method is being extended to include dielectric effects to model better grain boundaries in ionically-bonded ceramics.

PROCESSING-PROPERTY RELATIONS

J.E. Blendell, S. Block, T.W. Coyle, U.V. Deshmukh, E.R. Fuller, Jr., R.F. Krause, Jr., C.P. Ostertag, T.R. Palamides[1], G.J. Piermarini, L.C. Stearns, M.D. Vaudin, C.A. Harding, and C.A. Shen[2]

[1]Guest Scientist, Drexel University
[2]Summer Student, Massachusetts Institute of Technology

Ceramic Matrix Composites: Low and high-temperature mechanical performance and structural stability of ceramic matrix composites is controlled to a large extent by the structure, properties and stability of fiber-matrix interfaces. Techniques to characterize these interfacial properties and to relate them to both processing and macro-scale mechanical behavior are required to develop reliable ceramic composites. Experimental studies have been undertaken to develop the understanding necessary to bridge the gaps between processing, the nature of the fiber-matrix interface, and the performance of bulk composite materials. Three scales of behavior are examined: micro-mechanical behavior of individual fiber-matrix interfaces is characterized by an instrumented indentation technique; interactions of matrix cracks with simple arrays of fibers are investigated by a novel fracture-mechanics specimen with controlled fracture behavior; and the performance of bulk composites (uniaxial and woven-fiber reinforced materials and whisker-toughened materials) is examined for various failure modes. Although composites from external sources have been examined, much of the effort has centered on the development of a model composite system, composed of a borosilicate glass matrix containing SiC monofilament fibers. Specimens, designed for examination of the three scales of behavior, have been fabricated from these components using nearly identical processing conditions. These coordinated studies, conducted in collaboration with the Glass and Composites Group, permit the relations between processing and mechanical behavior at the three scales to be directly correlated.

Ceramic Superconductors: The interrelations between processing, microstructures, and properties is particularly important for the new high T_c ceramic superconductors. To elucidate these interrelations, $YBa_2Cu_3O_{7-x}$ superconducting ceramics (with x in the nominal range of 0 to 1) have been

fabricated, their properties measured and related to microstructure and processing conditions. Materials were prepared by powder processing techniques, followed by dry pressing and sintering in both air and flowing oxygen at various temperatures. Sintered bodies were annealed at various temperatures and environments to enhance superconducting properties, such as, transition temperature and transition width. These properties, as measured by electrical conductivity and AC magnetic susceptibility, as well as microstructure showed strong sensitivity to processing conditions: annealing atmosphere, temperature, and sintered density. Compositional mapping proved to be an important method for quantifying microstructure variations.

A major impediment to the use of high Tc superconducting ceramics is their brittleness, with a fracture toughness of only ~1.2 $MPa.m^{1/2}$. To enhance sintering, and hence structural properties, powder is milled to small particle sizes. During this process, the orthorhombic superconducting phase of $YBa_2Cu_3O_{7-x}$ underwent low-temperature chemical reactions with various milling media. The chemically modified powder has a tetragonal structure and is non-superconducting. The orthorhombic structure, and hence superconductivity, can only be fully regenerated by annealing at 950°C. In addition, these modified powders are extremely reactive with reinforcing fibers or whiskers, added to enhance the fracture toughness and strength.

<u>High-Pressure Transformation Toughening</u>: Transformation toughening is a well-known and effective method for enhancing the fracture toughness of ceramic materials. Transformation toughening by the retention of high-pressure metastable phases is a concept that originated at NBS. Criteria necessary for such toughening require the toughening agent to exist metastably at ambient pressures and temperatures and to have a rapid, reversible, pressure-induced, phase transformation. This new approach to toughening is currently being applied on a U.S. Navy program to develop tougher, infrared-transmitting missile windows. Such windows must consist of tough, relatively transparent nonoxide materials, such as chalcogenides or phosphides. Candidate samples from a number of sources have been studied in the diamond anvil cell. Six potential toughening agents, $T\ell I$, $T\ell GaSe_2$, $T\ell InS_2$, Gd_xSe_y, $SrNd_2S_4$ and Ag_3SbS_3, have been identified, the first three of which possess rapid, reversible transitions at low pressures (less than 500 MPa). Preliminary measurements on toughening ZnS with $T\ell I$ show a 30% toughness increase over hot-pressed materials.

<u>Transformation Toughening in ZrO_2</u>: Enhanced use of tetragonal ZrO_2 as a toughening agent requires a thorough understanding of the transformation thermodynamics and kinetics, especially the relative influence of mechanical versus chemical driving forces. In the past year, in collaboration with R. Ingel of the Naval Research Laboratory, temperature dependence of the fracture toughness, strength, and yield stress has been measured for an unstabilized, skull-melt grown crystals of ZrO_2 from room temperature to 1500°C. Results indicate a clear transition from yield controlled by dislocation slip at high temperatures to yield controlled by stress-induced transformation below 1200°C. Fracture toughness results indicate that a toughening mechanism is operative at temperatures, where the tetragonal phase is thermodynamically stable in the absence of a constraining stress.

Decomposition Kinetics of Energetic Materials: A Fourier transform infrared (FTIR) microspectroscopic method is used in conjunction with a diamond anvil cell to obtain pressure-temperature data for thermal decomposition kinetics of energetic materials, such as, RDX, HMX, TNT, and nitromethane. Current work involves the study of nitromethane, its reactivity and phase diagram. Although no new phases were found, under some conditions, single crystals at room temperature spontaneously explode with the application of nonhydrostatic stress. A deuterated analogue, on the other hand, did not explode. The decomposition reaction rate increased rapidly with both temperature and pressure, indicating a bimolecular-type reaction mechanism.

Ceramics Chemistry and Bioprocesses Group

Frederick Brinckman

In the past year the Ceramic Chemistry Group was joined with the Surface Chemistry and Bioprocesses Group. These Groups had both emphasized molecular level approaches to materials processing and performance. This joining has thus strengthened and centralized the respective expertise and facilities for molecular-level characterization, understanding and monitoring of chemical and biological processes important to inorganic, especially ceramic materials.

The Group conducts research in (1) the application of modern chemical approaches to improved processing of ceramics and (2) in chemical and microbiological processes important in materials processing, performance and durability. The objectives of the Ceramics Chemistry and Bioprocesses Group are to provide data, measurement methods, concepts and standard materials related to chemical aspects of ceramics processing, chemical and microbiological processing of ores, wastes and fossil fuels and performance of inorganic materials in service environments.

Representative Accomplishments

- Two different low temperature chemical precipitation routes to the high T_c Y-Ba-Cu-O superconductor material have been developed. After firing pellets of these materials at ~900°C and annealing in O_2 at 600°C, sharp transitions in resistivity and magnetic susceptibility were measured at ~86κ. These procedures represent an initial advance towards controlled synthesis of superconductive materials which are amenable to continuous intelligent processing.

- A convenient hermetically-sealed, inert atmosphere cell for x-ray powder diffraction was designed and developed. The unit is a "plug-in" device and requires no modification of existing service diffractometers for use. The cell provides protection for atmospherically sensitive materials, particularly the barium oxides and hydroxides used in superconductor preparations. Application for a U.S. Patent has been filed.

- Quantitative infrared profiles of Si_3N_4 preceramic powders were completed by generating working curves relating absorbance to concentration for α, β, amorphous materials. We now can analyze the morphological composition of Si_3N_4 via a single FTIR measurement: a technique of potential value for on-line ceramic process control.

- Demonstrated that 400°C pyrolysis of easily synthesized, ambiently stable polypyrazolyl- and polyimidazolylborates leads to amorphous boron nitride. Pyrolysis of lanthanide complexes containing the poly-BN ligands yields luminescent boron nitride precursor materials.

- Synthesized a new class of Si-N functionalized molecules that exhibit a rich coordination chemistry with metals in both low and high oxidation states. The coordination compounds are potential precursors

to silicon nitrides with unusual physical, optical, catalytic properties.

- Microbiological processing for metal recovery and ore beneficiation was demonstrated using industrially-supplied ores and wastes. Cobalt and nickel were leached from low grade ores and smelter wastes and insoluble phosphate minerals were removed from iron ore using specific microbiological reactions. Bioprocesses have the potential treatment and metal recovery from ores and wastes which are currently not economically recoverable using conventional technologies.

- Novel reactions of precious metal ions in aqueous solution with volatile biogenic metabolites were demonstrated. The metals were reduced to elemental powders in these reactions which have potential application in industrial metal recovery and separations, metal film deposition and powder production.

Ceramic Chemistry

J. J. Ritter, T. D. Coyle, R. A. Faltynek, T. K. Trout[1]

[1]Graduate Co-op Student, University of Maryland

Within the past year, we have developed several chemical precipitation routes to the high Tc, Y-Ba-Cu-O superconductive materials. Satisfactory powders of this material can be obtained by co-precipitating the metals as mixed-carbonates and hydroxides. An alternative route is derived from a heterogeneous interaction between the soluble barium and yttrium alkoxides and an insoluble copper alkoxide. The superconductive behavior of powders obtained by these procedures is summarized in figures 1 and 2. Satisfactory materials are also produced by precipitation of the metals as either complex citrates or oxalates from organic solvent systems. These different chemical systems are being evaluated as to their amenability to continuous powder production techniques and as to their adaptability to "intelligent processing" controls. The progress of our research in this area has been facilitated by our development of a convenient inert atmosphere x-ray diffraction cell since the calcined, precipitated Y-Ba-CuO powders tend to be moisture sensitive.

Synthetic studies have shown that families of compounds containing boron-nitrogen or silicon-nitrogen bonds are accessible from stable starting materials and that 400°C pyrolysis of these materials yields organic-free precursors to boron nitride and silicon nitride. Significantly, the compounds form coordination complexes with transition metal and rare earth ions, thus providing potential sources for ceramic powders containing optically or catalytically active sites locked into regular geometries as a consequence of the initial bonds in the coordination complexes prior to pyrolysis. For example, an amorphous boron nitride material pyrolytically synthesized from mixtures of a neutral B-N ligand and its coordination complex with terbium(III) retains the luminescence inherent in the coordination complex itself, supporting the above hypothesis.

Detailed Fourier Transform Infrared (FTIR) analysis of pure amorphous, α, and β-phase silicon nitride has yielded working curves relating absorbance to weight percent composition of the materials in an inert KBr matrix. Accordingly, it is now possible to determine the morphological profile of any mixture of the three phases of Si_3N_4 from one FTIR measurement. Since infrared analysis is faster and more convenient than traditional x-ray powder diffraction analysis, the FTIR technique offers the promise of rapid, on-line determination of phase conversions during Si_3N_4 processing.

Chemical processes and changes in molecular structure in "sol-gel" processing of silica by hydrolysis of TMOS were studied by a combination of small-angle x-ray and small-angle-neutron scattering with chromatographic techniques. Studies with specially-synthesized deuterated reagents revealed a significant but hitherto unreported isotope effect--a marked inhibition of the initial hydrolysis reactions in acidic and neutral, but not basic solutions. This observation provides potential insights into the mechanisms of chemically-based ceramic synthesis procedures that can be utilized for better process control and optimization. [The x-ray scattering studies were carried out in cooperation with the Oak Ridge National Laboratory.]

Microbiological Processing of Materials

G. J. Olson, F. E. Brinckman, K. L. Jewett, W. R. Blair, E. J. Parks, T. Trout[1], R. Blakemore[2], J. S. Thayer[3], R. M. Kelly[4], W. Su[4], W. P. Iverson[5], C. Sakai[6], J. Zelibor[6], D. Darnall[7], H. E. Guard[8]

[1]Graduate Co-op Student, University of Maryland
[2]Guest Scientist, University of New Hampshire
[3]Guest Scientist, University of Cincinnati
[4]Guest Scientist, The Johns Hopkins University
[5]Guest Scientist, Retired
[6]Guest Scientist, University of Maryland
[7]Guest Scientist, New Mexico State University
[8]Guest Scientist, Office of Naval Research

The Group's activities in this area provide critical data, standards and molecular measurement methods supporting the development of industrial processes using microbial transformation of inorganic materials. These activities are supported by the Office of Naval Research (bioprocessing of strategic elements), the Electric Power Research Institute (bioprocessing of coal), the Office of Standard Reference Materials, and the NBS Steel Research program.

In the past year we have demonstrated microbiological processing for the selective dissolution of cobalt and nickel from low-grade domestic ores (Duluth gabbro) and smelter wastes (with St. Joe Minerals Corp.) Such work has attracted the interest of the Idaho Mining Association. Following joint visits, we have begun consultations with members of that group and the Idaho National Engineering Laboratory to develop novel biological and chemical processes for precious metal recovery. Planning is underway for a major collaborative research activity to begin in the coming year. We are

also formally consulting with the U.S. Air Force in the development of new gallium biorecovery processes.

We have also evaluated different iron sulfide ores as suitable substrates for the production of a metal ore bioleaching standard and have generated data on reproducibility and processing variables associated with ore bioprocessing (Fig. 3). The international scientific and industrial community involved in developing bioleaching processes for ore bioprocessing has made repeated requests to us for standards in this area. Concurrently, we are writing standard procedures for conducting ore leaching tests within the Metal Ore Bioleaching task group (G. J. Olson, Chairman) of ASTM E-48 (Biotechnology). These procedures will form the basis for a planned international inter-comparison on determination of ore bioprocessing rates.

Under the steel research program we are investigating the upgrading of the major raw materials of steel making: the removal of phosphorus from iron ore and selective dissolution of copper and other deleterious metals from steel scrap. We have found that exocellular microbial metabolites play key roles in both of these processes. In the case of iron ore we have found that one or more exocellular metabolites from a fungus isolated from Chesapeake Bay dissolves insoluble phosphate minerals. We are currently determining the identity of the metabolite using liquid chromatography techniques. Our results have greatly encouraged Cleveland Cliffs Iron Co. in Michigan. They have huge iron ore reserves but are mining at only half capacity because these ores contain a relatively high concentration of phosphorus mineral which is not economically removable using current technology.

We are also identifying biogenic metabolites as agents for dissolution of copper and other impurities from steel scrap. We are investigating basic mechanisms and relative rates of aqueous dissolution of iron and copper from their metallic forms using iodomethane and other biogenic metabolites. Also under the Steel and Strategic Metals projects we are investigating prospects for direct aqueous reduction of metal ions to elemental powders through organometallic reactions. We showed that Pt, Pd and Au ions are reduced to their respective elemental states using aqueous and gas phase reactions with iodomethane and trimethyltin ion. Microbiologically generated gaseous metabolites were also shown to reduce plantinum ions to elemental platinum.

Microbes also affect the performance of materials in service environments. In this area we are evaluating for the U.S. Navy, the effect of microbiological films on the release of tributyltin (TBT) species from surfaces coated with TBT-based antifouling coatings with low release rates. Our work will identify the extent to which microbial films act as capacitors for the release of this biocide. This will influence the design and implementation of new antifouling coatings since paints with exceedingly low TBT release rates may be effective in preventing "hard" fouling of ships if the microbial film contains sufficient TBT to repel fouling larvae. Our non-destructive surface analysis capabilities of microscopic Fourier transform infrared spectroscopy and epifluorescence microscopy coupled with fluorescent tin ligands are assisting in imaging and quantitating tin in the biofilm.

Also related to TBT research, we are conducting for the U.S. Navy a new international measurement methods intercomparison for speciation of butyltin compounds. More than 130 laboratories in 21 countries have been invited to participate in the methods intercomparison.

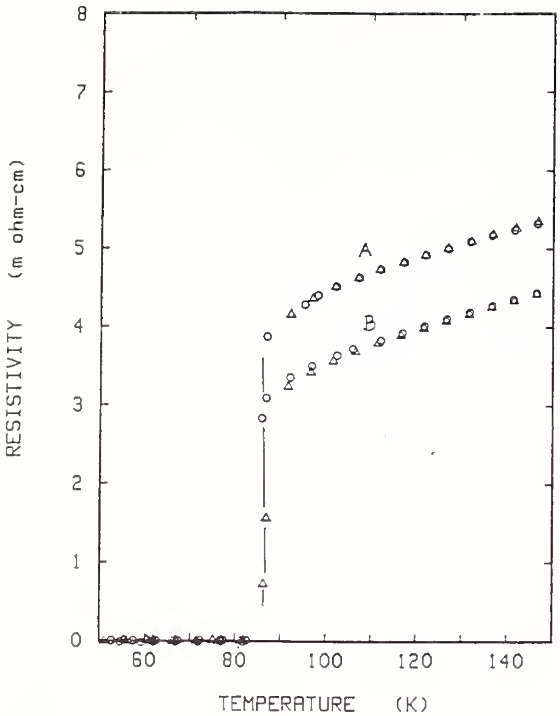


Figure 1. Resistivity vs. absolute temperature plots for chemically derived superconductor materials. A. mixed carbonate/hydroxide route; B. metal alkoxide route. Measurement performed by C. K. Chiang.

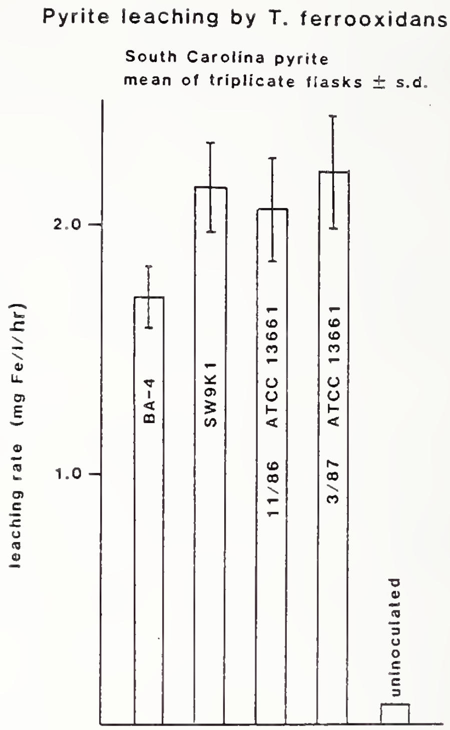


Figure 2. Rates of bioleaching of iron pyrite by three strains of the ore leaching bacterium <u>Thiobacillus ferrooxidans</u> (BA-4, SW9K1, ATCC 13661). Data on bioleaching measurement reproducibility is needed for standards development and for interlaboratory measurement comparisons.

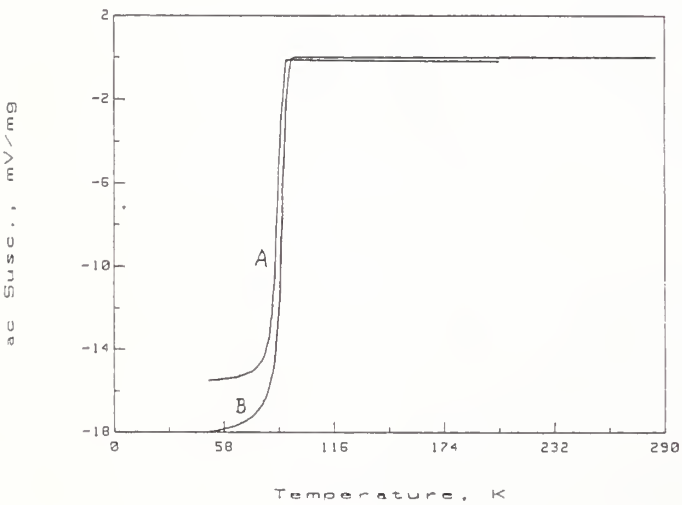


Figure 3. AC susceptibility vs. absolute temperature plots for chemically derived superconductor materials. A. mixed carbonate/hydroxide route; B. metal alkoxide route. Measurement performed by C. K. Chiang.

STRUCTURE/STABILITY

High Temperature Chemistry

John Hastie

Our research program in high temperature chemistry emphasizes the thermodynamic, chemical-kinetic, interfacial microstructure, and molecular-level behavior of inorganic materials in high temperature process and service environments. Specific current objectives are (1) to provide technical support to the Division's Ceramic Phase Diagram Data Program through critical evaluation and modeling of phase diagrams and the development of computer graphics for computer storage and manipulation of phase diagrams; (2) to support the U.S. Steel Industry through development of a thermodynamic database and solution model for prediction of slag, refractory, and inorganic steel inclusion thermochemistry; (3) to develop and apply (eg., to refractory ceramics and composites) a new molecular-specific methodology for obtaining thermal and chemical stability data at ultra-high temperatures (2000 - 5000°C) for design of hypersonic transport vehicles and various defense applications; recent surveys by NMAB and Industry have indicated a critical need for thermochemical and other materials property data at these temperatures; and (4) to obtain phase equilibria, kinetic, and mechanistic data for the development of stored chemical energy propulsion systems.

Representative Accomplishments:

- A prototype computer database and model has been developed for the oxide systems commonly present in steel making. The model has been disseminated to Inland Steel and several other industries for testing and application to process design. The generic basis of the model makes it applicable to both the blast furnace and refining phases of steel making.

- The laser-induced vaporization mass spectrometric technique has been further developed to include time and spatially resolved analysis of refractory vaporization. Local thermodynamic equilibrium conditions have been demonstrated using graphite and boron nitride materials at temperatures of 2700 - 3900°C; hence the method should be applicable as a new thermochemical tool under conditions not attainable by conventional methods.

- Using the technique of transpiration mass spectrometry (developed by NBS), the key reactions between ClO_3F and Al were identified. These reactions form the basis for new stored chemical propulsion devices under development by U.S. Industry.

Phase Diagram Graphics, Evaluation, and Modeling

P. K. Schenck, L. P. Cook, P. Davidson[1] and J. W. Hastie

[1]NRC Post Doc

New computer graphics software has been developed to handle complex binary and ternary diagrams using stand alone desk top computers. The publication-ready diagrams for the recently completed Vol 6 of "Phase Diagrams for Ceramists" were generated with this system. Software was also developed to provide PC-access to the ceramic phase diagram graphics data bank. PC-users will have the ability to retrieve data from the screen display and in a choice of user units (eg. °C, F, K, mole%, wt%). Mixture compositions can also be determined interactively by use of the lever rule and the results displayed on the PC-monitor screen.

Dr. L. Cook, in collaboration with an international panel of phase equilibria experts, has critically evaluated phase diagrams for molten salt systems. These diagrams will form the basis of Vol. 7 of "Phase Diagrams for Ceramists" which is expected to be completed in 1988.

Thermodynamic solution models, based on a generalized point approximation for the principal ternary solution phases in the system CaO, MgO, FeO, SiO_2, have been combined and optimized with respect to new thermochemical data on phase equilibria, solution enthalpies and long-range order. A model for pyroxene crystallization from silicate liquids treats new experimental data with several simple melt-models to predict crystallization temperatures and compositions that are within measured experimental and analytical errors.

Steel Slag - Refractory Thermochemistry

J. W. Hastie, D. W. Bonnell, E. R. Plante, and W.S. Horton[1]

[1]Contractor

Recent work has concentrated on developing a thermodynamic database for Fe-M-O phases (M = Al, Ca, K, Na, and/or Si) necessary to model complex steel slags. Thermochemical data are also under development for minority species such as iron sulfides, CaF_2, sulfates, and the oxides of chromium and titanium. The data- base for the previously developed NBS solution model now contains over 100 species (i.e. solid and liquid complex oxide components) for over 10 atomic constituents. A new technique is being developed, using silica self-associates, to model the positive deviations from ideal mixing which can occur in high silica-content phases.

New experimental thermochemical data have been obtained using Knudsen effusion mass spectrometry, for an Inland Steel Co. furnace slag specimen, in addition to synthetic slag samples. Data obtained on potassium partial pressures is a particularly sensitive measure of the oxide activities, as potassia forms a broad succession of strong complex interactions with all the slag oxides. The experimental thermodynamic activities obtained are being compared with the model predictions.

Laser-Induced Vaporization Mass Spectrometry

D. W. Bonnell, P. K. Schenck, and J. W. Hastie

The coupling of laser heating with mass spectrometric analysis has the potential for providing quantitative thermochemical data for refractory materials at temperature and pressure extremes heretofore inaccessible to equilibrium techniques. In addition, degradation of materials by high powered lasers is important in, for example, the design of laser fusion processes, laser welding, laser processing of ceramics (most recently, superconducting and diamond films), laser etching of semiconductor components, laser annealing of surface alloys, and in the durability of refractories in defense and space applications.

We have shown that a Nd/YAG laser system focused to power densities in the region of 10^8 W/cm^2, is a convenient energy source for producing controlled vapor plumes with generally negligible post-vaporization perturbation of the neutral species identities and concentrations. The NBS LIVMS technique utilizes time-resolved mass analysis to provide time-of-flight species specific information on temperature, neutral precursors, and time history of the laser heating process. The technique has been demonstrated on the BN system at temperatures around 2700°C and the graphite system at temperatures around 3900°C, and at total pressures in the vicinity of an atmosphere.

Stored Chemical Energy Systems

L. P. Cook, E. R. Plante, and D. W. Bonnell

A number of fuel/oxidant reactions are of current interest to DOD and Industry, including several which are multistage: Li/H_2O, Na_2O/H_2O, H_2/O_2; $MgAl/H_2O$, H_2/O_2; $LiAl/ClO_3F$; $LiAlMg/ClO_3F$; $LiBe/ClO_3F$; Li/ClO_3F; LiB/NF_3. Thermodynamic prediction of the products of three of these reactions has been corroborated by equilibration of postulated products at high temperature. Mass spectrometric observations on the thermal decomposition of ClO_3F have shown that O_2, Cl_2 and F_2 are the likely key reactants. Future work is planned which will determine rate constants and temperature dependencies for the kinetics of the oxidation of individual alloy components by Cl_2, O_2 and F_2. Phase equilibrium determinations will focus on the system Li-Al-Mg-O-F, with special regard to the entry of fluorine into oxide phases.

Thermogravimetric rate data, obtained on the oxidation of molten aluminum droplets by ClO_3F, indicate multiple mechanisms, possibly including the following steps: (1) nucleation and growth of AlF_3 precipitation sites; (2) edge growth of AlF_3 islands followed by coalescence of islands; (3) diffusion limited thickening of the AlF_3 layer. Observations on the early stages of the Al/ClO_3F reaction have also been made using high pressure sampling transpiration mass spectrometry.

SYNCHROTRON RADIATION

Masao Kuriyama

Important new materials in industry are produced by far more sophisticated processing methods than previously utilized. These materials are to be made with control of the buildup of layers designed at the atomic level. Success with such materials will require the knowledge of new ways to arrange the atoms in order to achieve the desired results. But such know-ledge, while important and necessary, is insufficient by itself. The structure of all materials when formed is non uniform locally often over regions of the order of a micrometer. Therefore, as important as, or possibly even more important than, novel materials design will be infor-mation on, and control of, these local variations in actual materials produced by atomistic design. The objective of the Synchrotron Radiation Group is to apply and improve the recent advances of synchrotron radiation diffraction imaging techniques to various advanced materials in order to develop the fundamental understanding of the effects of defects and hetero-geneity on device performance and product yields. This fundamental know-ledge will directly assist U.S. industrial scientists and engineers to make high quality advanced microcircuits and ceramics superconductors compet-itive in the world market. In this support for intelligent processing, the group's current mission emphasizes effort improving generic measurement methods and providing basic data that will lead to the production of ad-vanced materials with superior properties for devices of higher quality and improved reliability.

Representative Accomplishments

- o Successful establishment of research collaboration with a consortium and industry in the application of synchrotron radiation to opto-electronic materials characterization.
- o Successful Application of Advanced Microradiography with X-Ray Image Magnification to Dental Research (Sub-micron resolution has been reached even with thick samples.)
- o Reconstruction of the history of layering of atoms during crystal growth from synchrotron radiation data.
- o Development of a new oscillation topographic imaging technique for materials with unknown orientation and multigrained materials.
- o Development of state analysis (momentum resolved in the in-coming and outgoing x-rays) for the quantitative determinations of strain fields and misorientations as separate physical quantities.
- o Initiation of spatial chemical mapping of materials using fluorescence x-rays with 5 μm resolution.
- o Establishment of an exclusive EXAFS beam line at the NBS/IMSE synchrotron beam line at NSLS in collaboration with CEEE.

Diffraction Imaging for Process Control in Commercial Crystal Growth

M. Kuriyama, B. Steiner, R. C. Dobbyn, U. Laor[1] and H. E. Burdette

[1]Guest Scientist, Nuclear Research Institute, Israel

The uniqueness of the NBS/IMSE Synchrotron Radiation Beamline, X-23A at National Synchrotron Light Source (NSLS), Brookhaven, is based on unconventional parallel monochromatic beam optics combined with the distinctive advantage of the small source size of the NSLS storage ring. Diffraction imaging with this unique facility is leading to an understanding of various defects and strain fields and of their generation and interactions during crystal growth and subsequent device manufacturing. This capability now has attracted attention from industry in semiconductors and optoelectronic materials, such as EG&G, Grumman, Morgan Semiconductor, Rockwell and Westinghouse as well as from government laboratories, such as NASA and Night Vision Laboratory. The Synchrotron Radiation Group has become a member of a consortium, the Center for the Development of Commercial Crystal Growth at Clarkson University, working with members from industry. The group has also developed independent collaborations with individual industrial laboratories to establish research programs for advanced materials for the future. Several small business crystal growers, such as II-VI Incorporated and San Diego Semiconductor Inc, have also requested NBS assistance and collaboration for evaluation of growth processes. Westinghouse Research Laboratory has also proposed collaboration with the Synchrotron Radiation Group for advanced materials using nonlinear optics.

In this area, significant technical results include:

a) Undoped GaAs--cellular arrays of interacting dislocations (Figure 1), linear subgrain boundaries and their termination (the latter suggests precursor cleavages which have not been observed before).
b) Doped GaAs--four distinct regions of differing microstructure; complex faceted growth (Figure 2), circular striations, turbulent interactions between the two regions and linear arrays of dislocations close to the edge of boules.
c) CdTe--rectilinear features of microstructure, including crystals grown in the furnace designed for space use.
d) HgI_2--multigrained structure rotated around a common crystallographic axis [110], and dendrite-like patterns along two orthogonal <100> directions.
e) ZnCdTe and HgCdTe (epitaxy)--large strains in the epitaxial layers that mask the structure of the substrate and interfacial regions.

High Resolution Radiography: Applications to Biomedical Imaging

R. Dobbyn and M. Kuriyama

In collaboration with S. Takagi and L. C. Chow, Paffenbarger Research Center, American Dental Association, parallel beam microradiography with x-ray image magnification has been applied to dental hard tissues. This technique was developed in the laboratory of the Synchrotron Radiation Group and was applied to real time observation of dynamic phenomena in alloys under heat treatment. The objective of the present application was

to ascertain the limit of spatial resolution in practice in the observation of structural features within dental samples.
Some features which had been predicted to be less than 2 μm are clearly observed. There also are significant differences in the fine structure of the lesion in microradiographs obtained at different x-ray energies. This fact may be attributed to the crystalline nature of the microstructure.

Reconstruction of the History of Layering of Atoms During Crystal Growth

B. Steiner, M. Kuriyama, R. C. Dobbyn, U. Laor[1] and G. G. Long

[1]Guest Scientist, Nuclear Research Center, Israel

Detailed analysis of synchrotron diffraction images of three slices from a single high quality boule of bismuth silicon oxide (optoelectronic material) has led to an understanding of the origins of layering in the deposition of atoms during crystal growth. The visibility conditions of striations associated with layering as a function of diffraction index, hkl, in the reflection and transmission geometries decipher a detailed recording of periodic and aperiodic variation in the boule resulting from interactions between the growing boule and the flow in the melt. Factors identified for improved uniformity of such materials include: symmetry in the solidification arrangement, reduction of fluctuations in rotations and thermal stability, and chemical balance.

A New Oscillation Technique for Diffraction Imaging

B. Steiner, R. C. Dobbyn and M. Kuriyama

In contrast to white radiation Laue imaging, diffraction imaging with a monochromatic beam has much better sensitivity to crystal strains and misorientations. However, if a sample is not oriented crystallographically beforehand, or has multiple grains, the application of this technique becomes extremely difficult. When many samples must be assessed systematically in a short time period, this difficulty discourages materials scientists from the wide use of this high sensitivity and quantitative technique. In this project, a new oscillation technique has been developed to determine diffraction indices without prealignment and regardless of grains in a sample crystal. Misorientation of grains can be determined within less than 1/10 of a degree and twist axes of the misorientation can be obtained accurately. After these quantities are determined, detailed information on strains and defects can be obtained from each grain.

High Sensitivity and High Spatial Resolution Chemical Analysis

R. C. Dobbyn, D. R. Black and M. Kuriyama

In collaboration with Peter Pella, Center for Analytical Chemistry, selenium has been identified in human and bovine blood sera at a level of 8 ppb through energy dispersive x-ray fluorescence. This high sensitivity permits the determination of selenium at a level of 24 ppb in such systems with a 10% standard deviation. This technique displays greater sensitivity for the analysis of dilute solutions than previously obtained. Work to

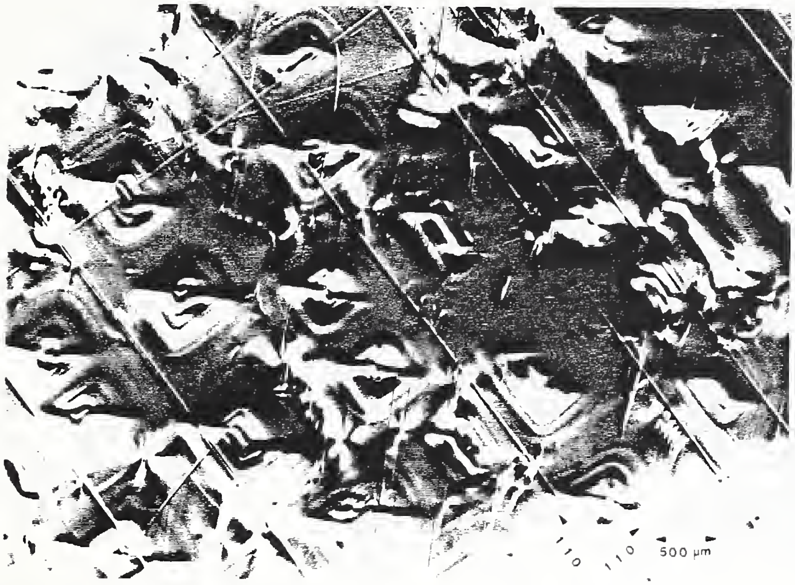
extend the spatial resolution for the compositional mapping to 5 μm is being initiated with flat crystal optics for fluorescence detection.

<u>X-Ray Monochromator Crystal That Detects the Bragg Condition</u>

R. Spal

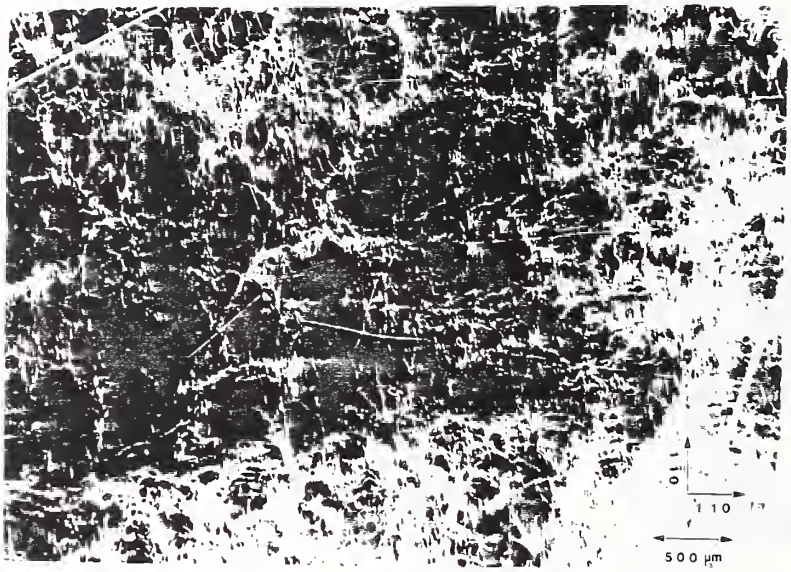
In collaboration with scientists from Center for Basic Standards and Center of Electronics and Electron Engineering, the feasibility of a self-aligning double crystal x-ray monochromator system has been demonstrated. An experiment with synchrotron radiation has confirmed that the voltage generated by a silicon crystal suitable for use in an x-ray monochromator is extremely sensitive to extinction at the Bragg angle. This signal can be used to orient a monochromator crystal quite accurately with respect to the Bragg angle.

Figure 5. Indium doped Gallium Arsenide



Enlarged portion of a transmission topograph ($0\bar{4}0$ diffraction) of a 800 micrometer thick indium doped gallium arsenide sample, R159-14 [CR2], taken at 10 kev on the NBS Materials Beam Line at NSLS. The central, faceted region of the slice shown here is surrounded by a peripheral region of growth striations characteristic of the growth. Other regions show the alignment of individual dislocations, along with dislocation-free regions.

Figure 4. Undoped Gallium Arsenide



Enlarged portion of transmission topograph (0$\hat{2}$2) diffraction) through an approximately 700 micrometer thick undoped gallium arsenide sample, GaAs-A1(100); [CG5], taken at 10 keV on the NBS Materials Beam Line at NSLS. Both individual dislocations and their entanglement, seen as cellular boundaries at lower resolution, are observed. This structure is char-acteristic of the entire crystal and of the two other undoped gallium arsenide samples studied.

GLASS AND COMPOSITES

Stephen W. Freiman

The Glass and Composite Group performs research in a number of areas, with a particular emphasis on the mechanical properties of glasses, polycrystalline ceramics, and ceramic matrix composites. There are major efforts being undertaken in the study of: (1) environmentally enhanced crack growth in brittle materials, (2) the effects of microstructure and chemistry on the fracture of polycrystalline ceramics such as those used in multilayer capacitors and the new superconducting ceramics (3) in the understanding of the fracture behavior of fiber-reinforced, ceramic-matrix composites. Data on the fracture behavior of brittle ceramics is needed in order to use these materials reliably in components which may be subject to mechanical or thermal stresses. Also, there is a considerable effort being placed in the development of non-destructive evaluation procedures for ceramics and ceramic matrix composites, with an emphasis on thermal wave analysis. In addition, there is ongoing work related to the development of glasses used as quantitative standards for elemental analysis. In all of these areas, the Glass and Composites Group is undertaking cooperative programs, both with personnel in other groups in the Ceramics Division, as well as with industrial and academic investigators in this country and abroad.

Representative accomplishments

- Environmentally enhanced crack growth was observed in GaAs single crystals for a variety of environments. These data have shown that models of environmental enhancement of crack propagation based solely upon bond ionicity are inadequate and must be extended. No subcritical crack growth could be observed in Si for a wide variety of chemical environments.

- Using thermal wave techniques, thermal diffusivity (α) values were measured for a set of dielectric materials. The measurements have shown that α can be determined reproducibly with an uncertainty of less than 10% using the photoacoustic effect (PAE). These results have been obtained in a cooperative program with AVX, a capacitor manufacturing company, which has provided samples for thermal, electrical, and mechanical tests. This collaboration provides NBS with custom made specimens to further research in dielectric ceramics and provides AVX with valuable data for the evaluation of electronic materials.

- The first data on the fracture behavior of superconducting ceramics has been obtained as a function of sintering and annealing conditions. The sensitivity of this material to moisture enhanced fracture was established.

- A fracture mechanics test procedure combined with a test designed to determine the interfacial strength between a SiC filament and a glass matrix were used to predict the effect of the filaments on retarding crack growth in ceramic matrix composites.

Environmentally Enhanced Fracture of GaAs and Si

G.S. White, S.W. Freiman, and A.M. Wilson[1]

[1]Summer Student, Oberlin University

Cracks were propagated in single crystal specimens of GaAs in environments with differing dielectric constants and chemical reactivities. Crack growth behavior was also correlated with x-ray topographs of the GaAs wafers. It was found that at least some of the strain patterns observed in the topographs corresponded to residual stresses in the wafers. Water, methanol and acetonitrile were observed to enhance crack growth in GaAs. In contrast, no crack growth was observed in ammonia gas. These results are at variance with a model which predicts that ammonia should be effective and acetonitrile ineffective in enhancing crack growth in materials whose bonds, like those in GaAs, are about 70% covalent in nature. Results from both macroscopic crack growth measurement techniques (double cantilever beam) and from microscopic techniques (indentation) provided quantitative ranking of the effectiveness of different environments in enhancing crack propagation with water being the most effective and methanol being the least. No chemical environment has been found which will promote crack growth in Si, which is 100% covalently bonded.

Thermal Diffusivity Determination Using Photoacoustic Techniques

G.S. White and C. Nguyen[1]

[1]Summer Student, University of Pennsylvania

In a cooperative effort of interest to the Navy, a set of barium titanate based dielectric specimens were obtained from AVX Corporation, and both Young's modulus, E, and thermal diffusivity, α, were measured at NBS. The work has been valuable to AVX because they have received data important in their evaluation of materials for electronics applications. E was measured using standard ultrasonic pulse-echo procedures. α was determined by fitting photoacoustic effect (PAE) measurements to a model in the literature. From measurements on a known (alumina) specimen, the model was found to predict α to within 10%.

Fracture of Superconducting Ceramics

D.C. Cranmer, S.W. Freiman, M.L. Balmer

Initial experiments aimed at characterizing the fracture behavior of the new high T_c $Ba_2YCU_3O_{7-x}$ superconductors were performed. Both fracture strength and fracture toughness were measured on samples sintered at 960°C in either air or oxygen and annealed at 600°C in either air or oxygen. Both the sintering and annealing environments were shown to affect strength and toughness. The highest strength and toughness was observed in as-sintered material fired in oxygen. Upon annealing both the strength and toughness dropped considerably. The fact that both K_{Ic} and σ show the same

trends indicates that the intrinsic properties of the material, not just the flaw population, are affected by the processing conditions. In addition, it was shown that moisture would enhance crack growth in these materials as it does in most other ceramics.

Phase Transformation Toughening of Thallium Iodide (TlI)-ZnS

D.C. Cranmer and S.W. Freiman

One mechanism for toughening ceramic materials involves the use of phase transformation toughening. This program is directed toward applying this mechanism of toughening to infrared transmitting windows. Because of its transmission in the 10-14 μM range, ZnS is a commonly used material in IR transmitting applications, but has a lower than desired value of K_{Ic} (1.0 $MPam^{1/2}$). TlI has a phase transition involving a volume expansion which occurs at 180°C, and a melting temperature of 440°C. Samples containing between 10 and 30 volume % TlI were prepared using reagent grade starting powders which were ball milled, pressed, and sintered between 375°C and 500°C. An indentation technique was used to measure both the hardness and the fracture toughness of the material. The best results were obtained with samples containing 20 v/o TlI. These samples were of low density compared to chemically vapor deposited material so that better results are expected for higher density samples.

Crack Growth in Capacitors Under the Influence of Electrical Fields

D.C. Cranmer, S.W. Freiman, and S. Chen[1]

[1] Summer Student, Duke University

A number of models exist in the literature which suggest that electric fields can alter the stress field at crack tips in electrostrictive ceramics. Depending on the material, orientation, and field strength, crack growth is either enhanced or inhibited. Crack lengths in the presence of an electric field between 0 and 300 V were measured using an indentation technique on X7R capacitors. Results suggest that crack growth in this material is inhibited by the presence of an electric field but that the effect is small (less than 10% change in crack length). Additional experiments are planned on materials having higher electrostrictive coefficients.

Fracture Behavior of Composites

T. W. Coyle[1], U. Deshmukh[2], T. R. Palamides[3], W. Haller[4], S. W. Freiman

[1] Processing Science Group,
[2] Post Doc,
[3] Graduate Co-op,
[4] Research Associate

The fracture strength and stress-strain behavior of continuous-fiber-reinforced ceramics is strongly influenced by the fiber/matrix interface. A primary goal of this program is to relate the mechanical properties of the interface to those of the composite. Special techniques have been devised to coat AVCO SiC filaments (SCS-6) with a slurry of glass particles and then quickly cure the slurry using high intensity ultraviolet radiation. The coated filaments are laid up uniaxially in a mold and hot pressed at 800°C to form composites containing ~25 volume percent of fibers. The mechanical behavior of the interface between individual fibers and the matrix has been characterized using a push out test. A special fracture mechanics specimen has been utilized to determine the effect of fibers in retarding crack growth.

PROPERTIES/PERFORMANCE

MECHANICAL PROPERTIES

Sheldon Wiederhorn

Our program on mechanical properties has as its broad objectives: (1) the generation of new theories and data to elucidate fracture and deformation mechanisms in brittle materials; (2) the development of fracture methodology for studying the fundamental forces that exist between two near surfaces; (3) the investigation of ceramic microstructure and its relationship to mechanical behavior; (4) the understanding of the deformation and fracture properties that govern the mechanical response of ceramics at high temperatures.

Representative Accomplishments

- A theory to explain the observed rising fracture toughness (R-curve) of monophase ceramic materials with growing crack size has been further developed. The source of the toughness of ceramic materials originates in interlocking grains and unbroken ligaments that cross between the crack faces. These apply a closure force to the crack that must be overcome for fracture to proceed. This theory implies that the toughness of ceramic materials can be enhanced by microstructural design to increase the degree of interlocking of fracture surfaces. Materials are currently being fabricated to optimize the toughness characteristics.

- The role of surface forces in subcritical crack growth has been explored for ceramic materials. Surface forces can account for a number of physical observations including the healing of cracks when the external driving forces are removed, and the presence of fatigue limits. These predictions are being investigated through experimental studies on mica, glass, and sapphire. A theoretical model of the role of surface forces has been developed.

- Creep in tension and compression have been shown to be unequal in high temperature structural ceramics suggesting the necessity for collecting creep data in both tension and compression for reliable design at elevated temperatures.

- A transient stress analysis has been obtained to characterize the creep behavior of structural components that are subjected to complex load configurations. The analysis technique has been applied to flexure specimens subjected to four-point bending, and to c-rings subjected to compressive loading. Asymmetric creep behavior was incorporated into the analysis.

Microstructure and Toughness

B.R. Lawn, S.J. Bennison[1], and H.M. Chan[1]

[1]Guest Scientist, Lehigh University

During the past year the strength behavior of a number of ceramic materials has been studied using indentation flaw techniques. Crack growth from the indentation flaws was recorded on a video tape recorder so that the

qualitative aspects of the intrinsic fracture resistance could be documented. The results suggest that interlocking grains and ligaments of unbroken material in the wake of the crack front serve to apply a closure force to the crack surface which must be overcome for the crack to propagate. Based on the above observations, a model of crack growth has been developed for predicting strength as a function of microstructure. The output of this project has strong implications concerning the microstructural tailoring required for optimum toughness properties of ceramics. A collaborative program with Dr. M.P. Harmer's ceramics processing group at Lehigh University is currently underway to explore this prospect. Monophase composites" are being made with duplex grain structures to provide maximum resistance to crack growth.

Surface Forces

B.R. Lawn, S. Lathabai[1], and R.M. Thomson

[1]Guest Scientist, Lehigh University

In addition to the covalent and ionic cohesive forces that hold brittle materials together, there are weaker (but longer-ranged) adhesive forces which come into play when new surfaces are created, particularly in the presence of interactive environments: dispersion (van der Waals), electric double layer, solvation and cation-site forces are examples. These are the surface forces which are of such great importance in colloidal chemistry. We have shown in fracture experiments on mica, glass and sapphire that forces of this type are important also in strength properties of ceramics. They bear on the reversible nature of crack growth (i.e. crack healing), and hence on the existence of a "fatigue limit," i.e. an applied stress level below which propagation ceases. This interrelation between surface closure forces and crack properties is leading to a fundamentally new conception of fracture, whereby the underlying processes of bond rupture <u>at</u> the crack tip operate independently of the adhesive processes <u>behind</u> the tip. Scientifically, the decoupling of the two processes provides impetus for study on crack-tip structures at the atomic level. More importantly, it offers a potential new technique for measuring surface forces using fracture. We have obtained experimental data on mica and other brittle ceramics, and have developed a theoretical model that relates the fracture behavior to surface force functions that can be measured by independent means.

High-Temperature Deformation and Fracture

S.M. Wiederhorn, T.-J. Chuang, B.J. Hockey, D.E. Roberts and D.F. Carroll[1]

[1]Guest Scientist, The Pennsylvania State University

The development of new ceramics provides hope for high efficiency, enhanced performance of structural systems in high temperature, stress-bearing environments. However, before ceramics can be used in industrial applications, issues concerning reliability and service life remain to be

resolved. With this in mind, we have been studying the creep and creep rupture behavior of model ceramics at elevated temperature.

During the past year the creep behavior of a commercial grade of reaction bonded silicon carbide was characterized at a temperature of 1300°C. Creep occurred more easily in tension than in compression. At a given applied stress, the steady state creep rate in tension was found to be at least twenty times that obtained in compression. In both tension and compression, the stress exponent for steady state creep was found to increase with increasing applied stresses. At low applied stresses, the stress exponent was ≈ 4, suggesting some kind of dislocation mechanism as a controlling factor in the creep of the two-phase composite. At high stresses, the stress exponent was ≈ 11. In tension, the increase in the stress exponent was attributed to damage accumulation in the form of cavities. An effective threshold stress for cavitation of less than 100 MPa was suggested. In compression, however, the cause of the increase of stress exponent with stress cannot be attributed to cavitation. A simple model has been proposed which is capable of describing all major features of the asymmetric creep. Data collected on this material are now being used to analyze distributions of stress and strain in ceramic components used in heat exchangers and in radiant heaters. During the coming year, data similar to these will be collected on other structural ceramics.

A new effort has been initiated to study the mechanical behavior of ceramic interfaces at elevated temperatures. Interfaces will be formed by the joining of ceramic materials at elevated temperatures, and the structure of these interfaces will be characterized by techniques of transmission and scanning electron microscopy. Once interfaces can be made in a reproducible manner, their strength and creep behavior will be studied under both normal and shear loads. Data obtained on this program will be used to characterize the mechanical behavior of ceramic joints in high temperature structural components.

TRIBOLOGY S. Jahanmir

Tribology is the science that deals with friction, lubrication and wear of interacting surfaces that are in relative motion. A prototype tribological contact consists of two solid bodies, separated by a thin film of lubricant, in a relative sliding motion; such as a bearing. This seemingly simple system is extremely complex and requires knowledge from several disciplines, such as materials science, physics, chemistry and engineering. The primary objectives of the Tribology Group are: 1) development of new theories and data to elucidate the complex reactions that occur between sliding surfaces and the environment, 2) exploration of mechanisms of friction, lubrication and wear of advanced ceramics, 3) establishment of test techniques and procedures for evaluating the performance of new materials, 4) generation of wear maps for materials to elucidate the effect of operating variables on performance, and 5) establishment of a computerized information system for tribology to be used for technology transfer.

Representative Accomplishments

- A time-resolved micro-Raman test system was developed to analyze chemical reactions at tribological contacts. The system uses a Nd-YAG laser to provide periodic pulses of monochromatic light which are focused on the tribocontact of a specially designed wear tester. This unique facility can provide fundamental knowledge on complex chemical reactions.

- The elucidation of chemical reactions between advanced ceramics and synthetic lubricants using a combination of tests showed strong chemical interactions between synthetic esters and alumina surfaces. Although the reaction products are essential for friction reduction, they may contribute to corrosive wear.

- Test results on alumina, silicon nitride and silicon carbide lubricated with mineral oil have shown that at a specific load both the friction coefficient and the wear rate increase to a level comparable with the data in unlubricated tests.

- Development of data to establish wear maps for advanced ceramics was initiated in conjunction with the Center for Advanced Materials at the Pennsylvania State University under the sponsorship of the Gas Research Institute. Wear maps for several advanced ceramics have been generated.

- The first public demonstration of a prototype model of A Computerized Tribology Information System (ACTIS) was successfully demonstrated. This paves the way for future effective technology transfer and potentially could save billions of dollars annually for U. S. industries.

In-Situ Analysis of Chemical Reactions

B.E. Hegemann and S. Jahanmir

The understanding of tribochemical reactions that control friction and wear has eluded researchers, partly because of the inability to observe the reactions in-situ and partly due to the inability to analyze the end results in a manner that would lead to the development of accurate models of the chemistry in the tribocontact zone. A time-resolved micro-Raman laser system was developed to elucidate tribochemical reactions occurring in the contact zone in real time. The system uses a Nd-YAG laser to provide periodic pulses of monochromatic light which are focused on the tribocontact of a specially designed wear tester. The scattered light is collected by specially designed optics and recorded by a gated intensified diode array detector. The detector system is governed by a device specified controller.

Ceramics Lubrication

J. M. Perez, C. S. Ku, P. Pei, L. S. Hsu and S. Jahanmir

The tribochemical reactions between several synthetic lubricants and ceramic substrates have been analyzed using unique facilities developed at NBS, which elucidate the chemical composition of surface films formed at tribological contacts. Results to date include: 1) differences were found in the rate of reaction of some synthetic lubricants with α-alumina. Although both a synthetic hydrocarbon and a polyol ester show good friction characteristics in the wear tests, decomposition products from the ester interact more readily with the substrate leading to a possible corrosive wear mechanism, and 2) two synthetic lubricants, a phosphate ester and a polyether both produce polymeric type reaction products which may be important to high temperature lubrication of ceramics.

Friction and Wear Measurements for New Materials and Lubricants

D.E. Deckman, R.S. Gates, J.P. Yellets, S. Jahanmir, and T.C. Ovaert

Ceramics are being considered for a wide range of applications in advanced heat engines that require high temperature performance. The research activities have focused on the selection of appropriate test apparatus, contact geometry, specimen preparation procedure, and assessment of the effect of test variables on friction and wear performance of several advanced ceramics. Test results on alumina, silicon nitride and silicon carbide, lubricated with mineral oil have shown that at a specific load both the friction coefficient and the wear rate increase to a level comparable with the data in unlubricated tests. The fundamental mechanisms which control this transitional behavior are currently under investigation.

To enable studies over a wider temperature range, two test apparatus have been developed to study friction, wear and lubrication characteristics of advanced ceramics. This facility was designed for temperatures up to 1500 degrees Celsius under controlled-atmospheres.

Wear Maps for Advanced Ceramics

R.G. Munro and D.S. Lim[1]

[1]Guest Scientist, University of Illinois

A comprehensive assessment was conducted on the tribological issues, research needs and priorities of ceramic materials relevant to engines fueled by natural gas. The assessment included a review of the technical literature, an appraisal of published data, and in-depth interviews and site visits to selected industrial research groups. The review concludes that data are needed in four general areas: performance, wear prediction, surface reactivity, and surface strength.

Advanced ceramic materials provide the key to developing high efficiency engines for which materials having high temperature stability, durability, and wear resistance are required. Data, design criteria, and an understanding of the effects of combustion products on the wear of materials are especially needed before ceramics can be fully utilized in advanced technology engines. Consequently, an effort was initiated to define the limits and requirements of ceramics under various conditions of speed, load, temperature, and environmental factors. These data are expected to provide a critical step towards understanding the wear mechanisms of advanced materials and the establishment of predictive models of wear.

A Computerized Tribology Information System

S. Jahanmir, R.G. Munro and S. Danyluk[1]

[1]IPA, University of Illinois

Research in tribology is attempting to reduce the estimated $100 billion cost incurred by the U. S. economy each year as a result of friction and wear processes. The Department of Energy has estimated that as much as forty percent of those losses could be saved by improved technology transfer. Research in tribology, however, is a complex, interdisciplinary effort that involves scientists and engineers of rather diverse areas of expertise. These researchers report their progress in correspondingly diverse media. As a result, advances in this field are often hindered by the inaccessibility of critical data or by the lack of awareness of parallel and concurrent research efforts.

An international effort to overcome this technological problem is being pursued through the development of A Computerized Tribology Information System (ACTIS). The central project, ACTIS, is an interagency government program sponsored by the Department of Energy/Energy Conversion and Utilization Technology/Tribology Program, the National Bureau of Standards, the U.S. Army/Fort Belvoir, the U. S. Air Force/Wright Patterson Aeronautical Laboratories, and the National Science Foundation. Additional support is being provided by the American Society of Lubrication Engineers, by the American Society of Mechanical Engineers, and by two distinguished advisory committees.

OPTICAL MATERIALS Albert Feldman

The objective of the Optical Materials Group is to provide data, measurement methods, standards and reference materials, concepts, evaluated data, and other technical information on the fundamental aspects of processing, structure, properties and performance of optical materials for industry, government agencies, universities, and other scientific organizations. The program supports generic technologies in crystalline, glassy, and thin film inorganic optical materials in order to foster their safe, efficient and economical use. Research in the group addresses the science base underlying new advanced optical materials technologies together with associated measurement methodology.

The principal area of optical materials research being covered is thin optical films, which addresses the processing/structure relationships of diamond and other ceramic coating materials and how they affect properties and optical performance as related to optical coatings and integrated optics.

Representative Accomplishments

o A diamond film deposition and characterization activity was begun. A diamond film deposition apparatus has been constructed and diamond films have been deposited. Structure in the films has been verified to be diamond as determined by x-ray diffraction, Auger electron-spectroscopy, electron energy loss spectroscopy, and Raman spectroscopy. Scanning electron microscopy indicates a significant surface roughness.

o The x-ray photoelectron spectra of the oxygen 1s and silicon 2p levels in films in the SiO_x system have been examined. Films prepared by reactive evaporation of Si in a partial pressure oxygen show silicon clusters and unincorporated oxygen. The composition of the remainder of the material agrees qualitatively with the random bond model (RBM).

o The photothermal radiometry signal vs chopping frequency from plasma sprayed films of zirconia and chromia has been fit to a mathematical model and values for thermal diffusivity and thermal conductivity have been obtained as a means for monitoring the quality of ceramic coatings. The thermal conductivities of the coatings appear to be two to five times smaller than the thermal conductivities of bulk materials.

Thin Optical Films

A. Feldman, E. N. Farabaugh, and Y. N. Sun[1]

[1]Guest Scientist, Lanzhou Institute of Physics, Lanzhou, Peoples Republic of China

Diamond Films: The Optical Materials Group has begun an activity in diamond film research. The emphasis has been on the deposition of diamond

films and identification of the diamond phase by a variety of methods. The electron-assisted CVD deposition method was chosen for its simplicity and for scale-up possibilities. Typical deposition parameters were: gas mixture, 0.47% methane, remainder hydrogen; flow rate, 50 sccm; deposition pressure, 40 torr; filament temperature, 1800°C (approx); substrate temperature range, 700°C; filament emission current, 0 to 10 ma.

Our first successful depositions were made on silicon wafer substrates. The deposited material consisted of crystalline particles having polyhedral shapes typical of the diamond particles described in the literature. Subsequently, we were able to deposit these particles on sapphire and silica as well. The size of the particles, as measured by SEM, were typically 3-10 μm. Micro-Raman spectra were obtained from individual particles by Edgar Etz of the Gas and Particulate Science Division. A sharp Raman line with very little background, centered at 1322 cm^{-1} which is 10 cm^{-1} below the Raman line of natural diamond, was observed. A measurement by Bob Nemanich of North Carolina State University on one of our later films showed the diamond line at 1331 cm^{-1} as expected. In addition, the latter spectrum showed a fluorescent background and additional graphitic-like structure near 1350 cm^{-1}. These results are typical of the best films he has measured. In order to deposit continuous films, we found it necessary to scratch the substrate surface with diamond paste.

X-ray diffraction measurements were made both with a Read thin-film diffraction camera and with a powder diffractometer. A one-to-one correspondence between the diffraction lines in natural diamond abrasive powder and the diffraction lines in the film was found. The lattice spacings of the film agree well with the lattice spacings of natural diamond.

Both our diamond films and graphite powder have been examined by Auger electron spectroscopy and by electron-energy loss spectroscopy. Based on the published results for bulk diamond and graphite, both sets of spectra confirm that our films are diamond.

<u>Thin Film Stoichiometry</u>: X-ray photoelectron spectroscopy (XPS) measurements of the O 1s and Si 2p lines in films of the SiO_x system have been interpreted on the basis of the random network model. Fitting of the spectra to five lines corresponding to five silicon centered tetrahedral configurations yield the relative proportion of each tetrahedron in the film. The distributions agree neither with the random mixture model (RMM) nor with the random bond model (RBM). The total oxygen in the films exceeds the amount of oxygen in the tetrahedral structures indicating the presence of molecular oxygen, water, peroxy bonding or other forms of oxygen not bonded to silicon. The general features of the distributions can be explained on the basis of silicon clusters, unincorporated oxygen and the RBM.

Photothermal Radiometry for Monitoring of Ceramic Film Quality

H. P. R. Frederikse, A. Feldman, and X. T. Ying[1]

[1]Guest Scientist from Fudan University, Shanghai, Peoples Republic of China

We have applied the method of photothermal radiometry to determine the thermal behavior of two different oxide coatings: chromia and partially stabilized zirconia, both deposited on aluminum plates. The oxide coatings were produced by arc plasma spraying in thicknesses ranging from 61 μm to 152 μm. A least squares method was used to determine the photothermal parameters which in turn yielded the values for thermal diffusivity and thermal conductivity. Table 1 lists the values obtained for both the chromia and the zirconia samples. In the last column we have listed some thermal conductivity figures quoted in a recent data handbook. The handbook values cover a large range because the thermal conductivity even of bulk ceramics depends strongly on the density, grain size, and purity of the material. Our measured results for plasma sprayed coatings appear to be at the lower end or just below the Handbook values. The considerable variation in magnitude confirms our expectation that the thermal properties of plasma sprayed coatings are strongly affected by the deposition procedures and conditions. It is quite possible that the thermal conductivity depends more on the contact resistance between the grains than on the conduction through the grains. The thermal wave method appears to have considerable potential for testing the thermal behavior of coatings. Because it is a non-contact technique, its use as an *in-situ* measurement at high temperatures appears to be practical.

Table 1. Summary of Thermal Diffusivities and Thermal Conductivities

Sample	thickness (μm)	thermal diffusivity (cm^2/sec)	thermal conductivity (W/cm deg)	thermal conductivity [Handbook*]
Cr_2O_3 - #1	100	0.013	0.0835	0.10 - 0.33
Cr_2O_3 - #2	150	0.014	0.0695	
Cr_2O_3 III	90	0.025	0.082	
Cr_2O_3 IV	125	0.015	0.063	
ZrO_2 A	60	0.017	0.007	0.018 - 0.022 (partially stabilized)
ZrO_2 B	97	0.017	0.012	0.0069 - 0.024 (plasma sprayed)

* "Ceramic Source '86" (Am. Ceramic Soc.), pp. 350-351.

COMPUTERIZED DATA ACTIVITIES GROUP Camden R. Hubbard

A rapid increase in new applications of advanced ceramics depends to a great extent on providing design engineers and research scientists with reliable and timely data compilations. The objective of the Computerized Data Activities Group is to meet this need in the fields of phase equilibria and materials properties of high technology ceramics. There are three subtasks within the Group: the Ceramic Phase Diagram Program; Phase Equilibria and Crystal Chemistry; and Ceramic Property Data.

The largest subtask is the Ceramics Phase Diagram Program which is conducted jointly with the American Ceramic Society. Closely related is the experimental Phase Equilibria and Crystal Chemistry subtask. These two activities are coupled to the measurement and prediction of x-ray powder diffraction reference patterns, a subtask within the Powder Characterization Group. The newest subtask is the assessment of needs for and initiation of activities leading to a national ceramic properties database system.

A materials property data program is of importance to our country's ability to introduce advanced ceramics competitively in the rapidly growing international advanced ceramic market. The activities of the last year focused on assessing the needs and opportunities in this field. Considerable encouragement has been received from the Gas Research Institute and from industrial representatives. Plans are to further emphasize this activity by expanding NBS' role in this field.

Representative Accomplishments:

- Completed evaluation, database entry and typesetting of Volume 6 of Phase Diagrams for Ceramists. This is the first evaluated data compilation from the NBS managed Ceramic Phase Diagram Program.

- Developed and exhibited at ACerS meetings a personal computer prototype phase diagram graphics package.

- Developed an oxide phase equilibria predictive capability which permits extrapolation into regions where experimental data are sparse and projection of isothermal surfaces and/or constant composition cross sections is required.

- Reported the structure, crystal chemistry, and x-ray powder diffraction reference patterns of the $BaO-Y_2O_3-CuO$ high T_c superconductor phase.

- Determined the phase equilibria relationships in the $BaO-Y_2O_3-CuO_x$ system in air near 900 C, and outlined the primary phase field of the superconducting phase.

- Evaluated the phase stability of the high T_c superconductor material in contact with potential container materials.

- o Assessed the needs for, materials to include, properties of interest, and service conditions for inclusions in a ceramic materials property database covering applications involving use of natural gas.

Ceramic Phase Diagram Program

C. R. Hubbard, H. M. Ondik, R. S. Roth, M. A. Clevinger, P. K. Schenck[1], L. P. Cook[1], J. H. Hastie[1], J. Dennis[2], T. Brittle[2], J.-O. Andersson[2], C. Messina[2], H. F. McMurdie[2], S. Cauley[3], P. O'Neil[3], M. Rodtang[3], D. Pennington[3], R. Wilson[3], and R. Yang[3].

[1]High Temperature Chemistry Group
[2]Research Associate, American Ceramic Society
[3]Student Research Associate, American Ceramic Society

The National Bureau of Standards (NBS)-American Ceramic Society (ACerS) ceramic phase diagram program completed its second full year of the expansion plan. This joint program is the response to industry's growing need for broad coverage of ceramic systems and a more current, evaluated data compilation. The need for these data is evidenced by industrial contributions of nearly $2,000,000 to support Research Associates at NBS who are responsible for the production of both computer databases and printed compilations.

(a) Phase Diagram Evaluation and Production. The first evaluated data output from the program, Volume 6 of Phase Diagrams for Ceramists, was completed and turned over to ACerS for printing. This volume contains 697 commentaries and 1080 binary, ternary and higher order phase diagrams of oxides, metals plus oxides, and metals plus oxygen. The completion of this Volume, produced using computer graphics and database systems, is a major milestone which sets the stage for numerous outputs of the Data Center.

(b) Database Development. The production of Volume 6 demonstrated application of all aspects of the database system and software established over the last two years. The most recent program addition was graphics entry procedures for ternary and partial diagrams. The commentary and bibliographic database software was fully tested and refined. The computer typesetting of the commentaries and indexes for Volume 6 was completed using recently completed software. The composition system operator has only to perform pagination and insertion of page headings.

(c) Computer Database Dissemination. To investigate means to enhance dissemination, two personal computer (PC) projects have reached the demonstration stage. A PC graphics package, which combines software and a graphics database, was exhibited at the ACerS Annual Meeting. This package permits the user to display any diagram from our database on a PC, to magnify regions (see Figure 6), to overlay related diagrams, to perform lever rule calculations, to display the cursor position in real units of the diagram, and to select the temperature scale. A second PC package demonstrated the successful transfer of commentary and chemical system data files from a minicomputer to a PC database management system and produced a comprehensive, PC searchable file.

(d) Modeling/Optimization. The Thermo-Calc program, developed at the Royal Institute of Technology in Stockholm, has been installed at NBS, successfully tested, and used to assess the role such modeling programs can play in the evaluation and dissemination of phase diagrams. Of great interest is the ability to generate particular cuts through high order diagrams (e.g. isothermal cuts of a ternary or higher order system). The program can be used to also predict approximate diagrams for systems with limited experimental data. Application to binary and ternary systems containing BaO, TiO_2, Al_2O_3, and MgO have shown good agreement with known diagrams and thermodynamic data.

Phase Equilibria and Crystal Chemistry

R. S. Roth, J. Dennis, K. Davis[1], J. Whitler[1], R. J. Cava[2], H. Parker[3], P. K. Davies[4], W. Wong-Ng[5]

[1] Student
[2] Guest Scientist, AT&T Bell Laboratories
[3] Guest Scientist, NBS
[4] Guest Scientist, University of Pennsylvania
[5] Guest Scientist, University of Maryland

Phase equilibria data supply fundamental information for the understanding of processing and stability of ceramics. This subtask focuses on measurement of the phase equilibria of important advanced ceramic systems such as microwave dielectric ceramics and the new oxide high T_c superconductors. Fundamental predictive information is developed from detailed crystal chemical and lattice defect information.

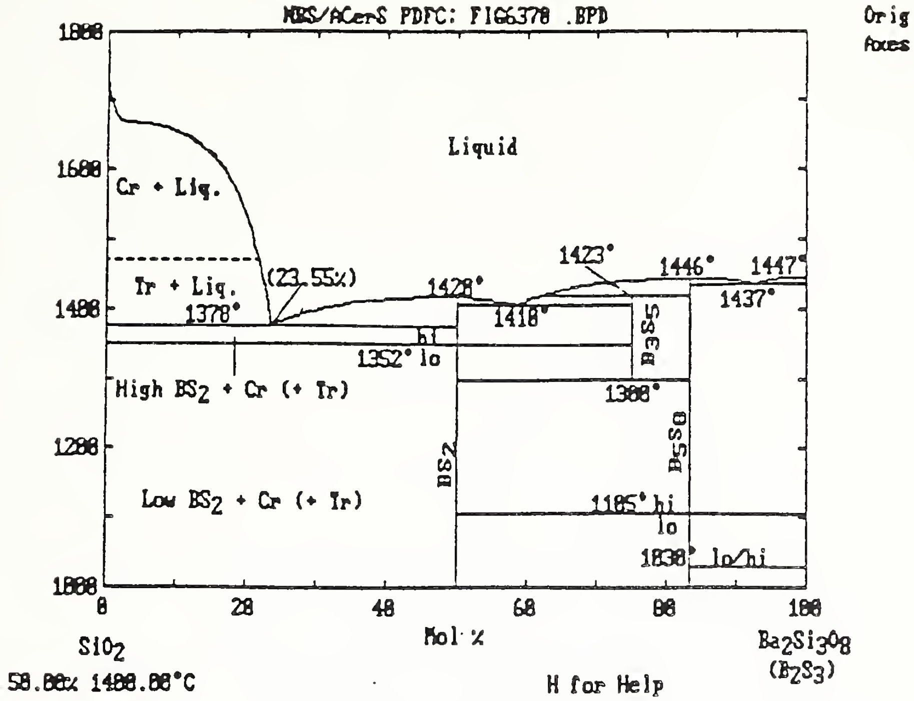
(a) $BaO-Y_2O_3-CuO$ Superconductor System. Preliminary phase equilibria diagrams were determined and reported for the three binary systems and the ternary system (Figure 7). Melting point data were used to outline the primary phase field, the composition region where single crystals of the $Ba_2YCu_3O_{7-x}$ superconductor (2:1:3) can be grown. The crystal chemistry of this phase was determined using neutron Rietveld analysis methods (see cover); X-ray powder diffraction reference data for the phases of this system were also reported.

(b) Container Reactions with melts in the $BaO-Y_2O_3-CuO$ System
Starting materials in the $BaO-Y_2O_3-CuO_x$ system are very reactive and corrode most common container materials potentially used in phase equilibria work and potentially processing. Experiments were conducted to test a Ag-Pd alloy, and preliminary results indicate that the alloy does not interact with the samples. Containers of this alloy were used to determine the melting relations near the 2:1:3 superconductor phase.

Ceramic Property Data

C. R. Hubbard

In collaboration with the Gas Research Institute, an assessment of the current status of computerized materials properties databases was conducted. The study found only nine mature and developing public domain, numerical, computerized data bases. Comparing essential design properties for selected gas fired applications with the coverage of these nine databases revealed very little overlap with the property data needs of design engineers. Identified barriers to developing a ceramics property database include materials specification, standardized test methods, and development of a database management system for scientific data. To address the first barrier, the task group on Specification of Ceramics of ASTM E49, on Computerization of Materials Property Data, met at NBS to focus on potential options.



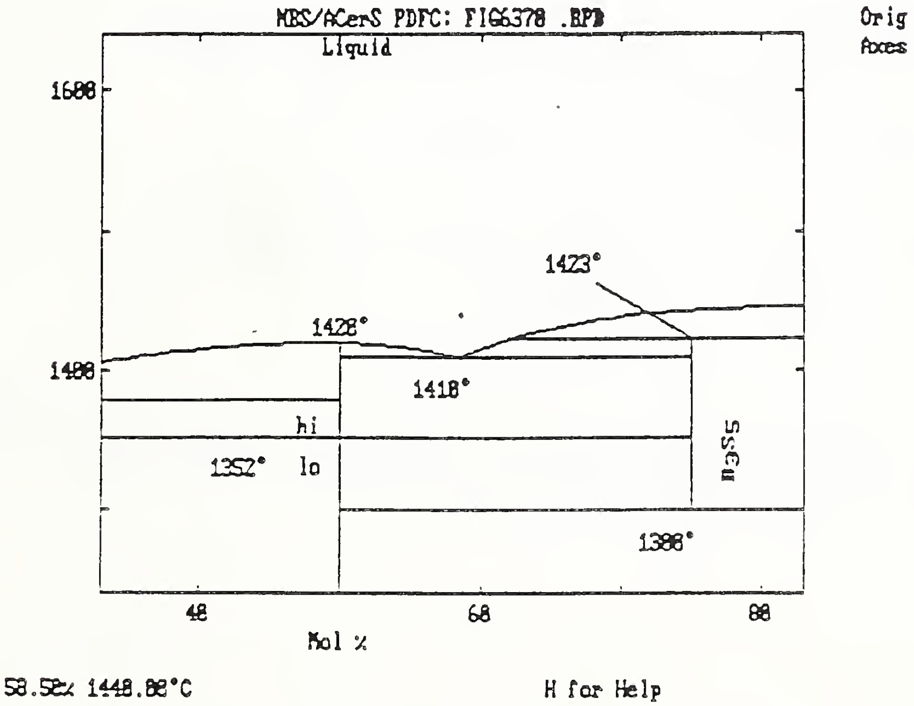


Figure 6. Copies of PC screens from the prototype PDFC graphics system. a) The SiO_2-$Ba_2Si_3O_8$ binary diagram. b) Section of the same diagram after magnification. Readout of the cursor position (+), in real units of the diagram, is shown at the lower left. A user-friendly help screen consisting of options available to the user is obtained by pressing the H key.

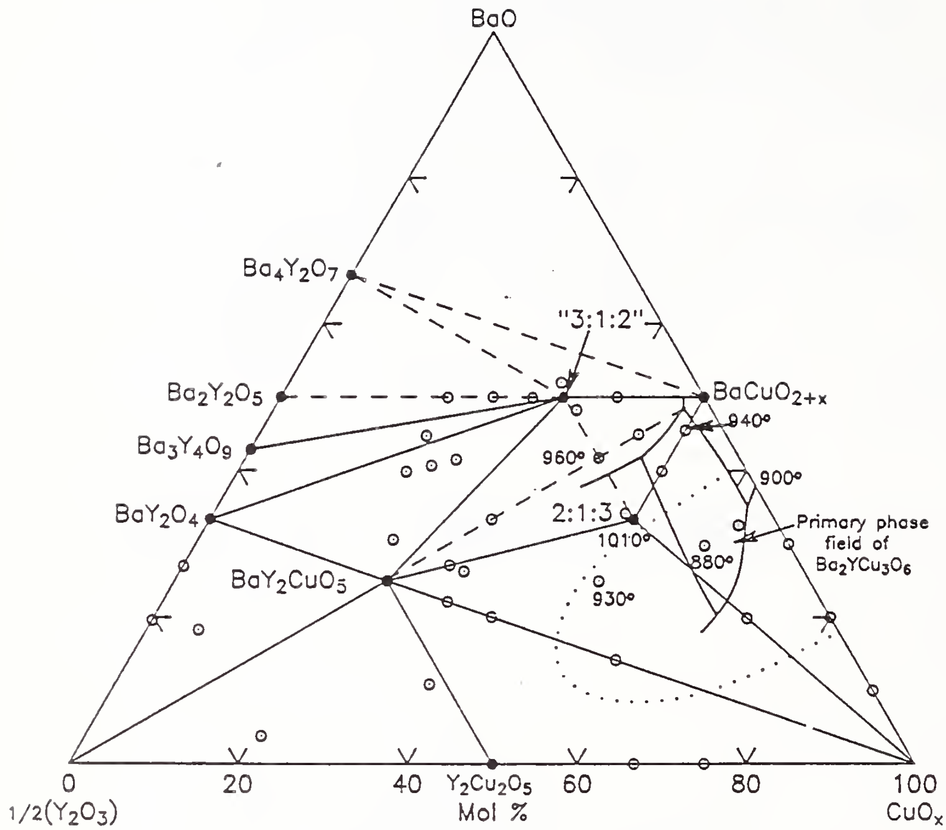


Figure 7. Phase diagram for the $BaO-Y_2O_3-CuO_x$ system in air near 900 C. The high T_c superconductor phase is labeled 2:1:3. The region where single crystals can be grown from a melt is the primary phase field.

RESEARCH STAFF

PROCESSING

Ceramic Powder Characterization

Cline, James P.	o X-ray diffraction of ceramics o Quantitative analysis
Dragoo, Alan L.	o Characterization of ceramic precursor powders o X-ray characterization o A-C spectroscopy
Kelly, James F.	o Scanning electron microscopy o Image analysis o A-C spectroscopy
Long, Gabrielle	o Small angle neutron scattering o Small angle x-ray scattering
Minor, Dennis B.	o Analytical SEM of ceramics and particulates o Powder test sample preparation o High temperature ceramic synthesis
Robbins, Carl R.	o Ceramic powder characterization o Spray drying; powder preparation o Quantitative microscopy and x-ray diffraction o NDE of ceramics

Processing Science

Blendell, John E.	o Ceramic processing and clean-room processing o Sintering and diffusion controlled processes o Processing high T_c ceramic superconductors o Activation chemical analysis
Block, Stanley	o Ceramic processing and high-pressure sintering o Pressure-induced transformation toughening o High-pressure physical properties & structures o High-pressure X-ray diffraction and spectroscopy
Coyle, Thomas W.	o Processing/microstructure/fracture relations o Toughening mechanisms in ceramics o Processing and properties of ceramic composites o Stress induced transformations

Fuller, Edwin R. Jr.	o Atomistic models of fracture and grain boundaries o Processing and properties of ceramic composites o Toughening mechanisms in ceramics o Processing high T_c ceramic superconductors
Harding, Chester A.	o Ceramic processing and sintering o Hot pressing o Ceramic fabrication
Krause, Ralph F. Jr.	o Fracture mechanics of ceramics o Creep of ceramics and high-temperature measurements o Chemical thermodynamics
Ostertag, C.P., Dr.	o Influence of heterogeneities on sintering o Processing and sintering of reinforced ceramics
Piermarini, Gasper J.	o Ceramic processing and high-pressure sintering o Pressure-induced transformation toughening o High-pressure physical properties & structures o High-pressure X-ray diffraction and spectroscopy
Stearns, Laura C.	o Ceramic processing and sintering o Electronic properties of ceramics
Vaudin, M.D., Dr.	o Microstructural properties of ceramics o Microscopy and diffraction of interfaces

Ceramics Chemistry and Bioprocesses

Blair, William R.	o Ultratrace metals speciation o Biotransformations of metals o Environmental durability of coatings o Molecular surface characterization
Brinckman, Frederick E.	o Environmental metal transport o Organometallic chemistry o Biological mediation of surface chemistry o Ultratrace metal speciation
Coyle, Thomas D.	o Inorganic and organometallic chemistry o Chemistry of materials processing and durability o Low temperature synthesis of ceramic powders o Chemistry of ceramic precursor materials

Faltynek, Robert A.	o Inorganic molecular synthesis o Surface and solution photochemistry o Spectrophotometry o Heterogeneous catalysis
Jewett, Kenneth L.	o Redox kinetics of heterogeneous systems o Organometallic speciation o Abiotic transformation of metal species o Analysis of organic mixtures
Olson, Gregory J.	o Metals biotransformation o Bioprocessing industrial materials o Epifluorescence microscopy imaging o Surface modification and bioadhesion
Parks, Edwin J.	o Metalloorganic synthesis o Macromolecular organometallic chemistry o Metals imaging in coatings o Ultratrace metal speciation o Biological transformation of inorganic materials
Rhyne, Kay A.	o Ceramic processing o Neutron scattering o Nondestructive analysis o Colloid and sol-gel chemistry
Ritter, Joseph J.	o Synthetic inorganic chemistry o Ceramic powders from organometallic precursors o Ceramic powders from gas phase, and solution precipitation reactions

Ceramics Chemistry and Bioprocesses

Blair, William R.	o Ultratrace metals speciation o Biotransformations of metals o Environmental durability of coatings o Molecular surface characterization
Brinckman, Frederick E.	o Environmental metal transport o Organometallic chemistry o Biological mediation of surface chemistry o Ultratrace metal speciation
Coyle, Thomas D.	o Inorganic and organometallic chemistry o Chemistry of materials processing and durability o Low temperature synthesis of ceramic powders o Chemistry of ceramic precursor materials
Faltynek, Robert A.	o Inorganic molecular synthesis o Surface and solution photochemistry o Spectrophotometry o Heterogeneous catalysis
Jewett, Kenneth L.	o Redox kinetics of heterogeneous systems o Organometallic speciation o Abiotic transformation of metal species o Analysis of organic mixtures
Olson, Gregory J.	o Metals biotransformation o Bioprocessing industrial materials o Epifluorescence microscopy imaging o Surface modification and bioadhesion
Parks, Edwin J.	o Metalloorganic synthesis o Macromolecular organometallic chemistry o Metals imaging in coatings o Ultratrace metal speciation o Biological transformation of inorganic materials
Rhyne, Kay A.	o Ceramic processing o Neutron scattering o Nondestructive analysis o Colloid and sol-gel chemistry
Ritter, Joseph J.	o Synthetic inorganic chemistry o Ceramic powders from organometallic precursors o Ceramic powders from gas phase, and solution precipitation reactions

STRUCTURE/STABILITY

Glass and Composites

Balmer, Mari Lou	o Mechanical Property Testing o Fiber processing
Blackburn, Douglas H.	o Special glass formulations o Glass processing o Glass standards for microprobe analysis
Cellarosi, Mario J.	o Glass SRM development o Glass standards for manufacture and use o Glass property measurements
Chiang, C. K.	o Electronic ceramics o Superconductivity
Cranmer, David C.	o Composites o Glass viscosity o Fracture
Freiman, Stephen W.	o Ceramics and glasses o Electronic ceramics o Mechanical properties, environmental effects o Composites
Kauffman, Dale	o Glass processing o Viscosity measurements
White, Grady S.	o Ceramics and glass o Nondestructive evaluation o Subcritical crack growth

High Temperature Chemistry

Bonnell, David W.	o High Temperature-pressure mass spectrometry o Computer modeling o Levitation calorimetry
Cook, Lawrence P.	o Phase equilibria of ceramics (modeling and experiment) o Phase diagrams for ceramists data center o Electron microscopy o Thermodynamics
Davidson, Paula M.	o Phase equilibria models o Thermodynamics

Hastie, John W.	o High temperature chemistry of ceramics o Ceramic phase equilibria and solution models o High temperature-pressure mass spectrometry o Chemistry of combustion
Plante, Ernest R.	o High temperature chemistry of ceramics o Knudsen effusion mass spectrometry o Vaporization thermodynamics
Schenck, Peter K.	o Laser spectroscopy o Temperature measurement o Computer graphics

Synchrotron Radiation

Black, David R.	o Inelastic x-ray scattering o Energy dispersive diffraction o Fluorescence and absorption
Burdette, Harold E.	o X-ray optics engineering o Crystal growth o Instrumentation
Dobbyn, Ronald C.	o X-ray imaging o X-ray optics o Microradiography
Kuriyama, Masao	o Scattering physics o Condensed matter physics o Crystallography
Spal, Richard D.	o X-ray optics o X-ray image detectors o Condensed matter physics
Steiner, Bruce W.	o X-ray diffraction imaging o Optoelectronic materials o Crystal growth

PROPERTIES/PERFORMANCE

Mechanical Properties

Chuang, Tze-jer	o Ceramics o Diffusional crack growth o Finite element analysis o Creep theory
Hockey, Bernard J.	o Ceramics o Scanning and transmission electron microscopy o Interfaces o Microstructure
Lawn, Brian R.	o Microstructure/strength relations o Fracture mechanics o Contact phenomena o Surface forces in fracture
Wiederhorn, Sheldon M.	o Ceramics o Fracture o Reliability o Creep rupture

Tribology

Hegemann, Bruce E.	o Time-resolved micro-Raman spectroscopy o Micro-FTIR spectroscopy o Laser-induced fluorescence spectroscopy
Hsu, Lin-Sien	o Lubricant volatility and oxidation stability o Lubricant fractionation o High temperature lubrication
Jahanmir, Said	o Wear mechanisms o Boundary lubrication o Mechanical behavior of materials
Ku, Chia-Soon	o Lubrication of ceramics o Lubricant oxidation, thermal stability and volatility o Lubricant degradation mechanisms
Munro, Ronald G.	o Theory and modeling o Molecular dynamics of phase stability o Temperature modeling of ceramic pairs
Pei, Patrick	o Characterization of lubricants and lubrication products o Separation of complex organic mixtures o Trace organic compound identification

Perez, Joseph M.	o Additive chemistry and deposits o Thermal and oxidation stability of fluids o Fuels, lubricants and diesel engines

Optical Materials

Farabaugh, Edward N.	o Thin film deposition and analysis o X-ray diffraction analysis o Scanning electron microscopy o Surface analysis o Diamond films o Superconducting films
Feldman, Albert	o Optical films o Guided waves o EXAFS o Diamond films o Superconducting films
Frederikse, Hans P. R.	o Thin film thermal wave analysis

Computerized Data Activities

Dennis, Jennifer	o Phase equilibria of ceramics o Electron microprobe o Phase diagram evaluation
Hubbard, Camden R.	o X-ray microstructural characterization o Reference data for ceramics o Crystal structure and chemistry o Database management
Ondik, Helen M.	o Phase diagrams for ceramists o Materials properties data o Database management systems
Roth, Robert S.	o Crystal chemistry of ceramics o Phase equilibria o Dielectric and electronic ceramics o Phase Diagram evaluation

GUEST SCIENTISTS AND GRADUATE STUDENTS

Andersson, J.-O., Dr.	Royal Institute of Technology, Stockholm
Bailey, David R.	The Pennsylvania State University
Baker, Theresa L., Ms.	Ohio State University
Bennison, S.J., Dr.	Lehigh University
Blakemore, R., Dr.	University of New Hampshire
Bretz, M., Dr.	University of Maryland
Carroll, D.F., Dr.	The Pennsylvania State University
Cava, R., Dr.	AT&T Bell Labs
Chan, H.M., Dr.	Lehigh University
Chen, C.F., Mr.	University of Michigan
Chen, Sharon, Ms.	Duke University
Cho, Seong-Jai	Korea Standards Research Institute
Craig, C.H., Mr.	Department of Defense
Darnall, D., Dr.	New Mexico State University
Davies, P., Dr.	University of Pennsylvania
Davis, K.	University of Maryland
Deckman, Douglas E.	The Pennsylvania State University
Degnan, T., Dr.	Mobil Oil Company
Deshmukh, U., Dr.	Drexel University
Dong, Jie-Yi	East China University of Chem. and Tech.
Dong, Xiaoyuan	Tsinghua University
Eng, G., Prof.	University of the District of Columbia
Gates, Richard S.	The Pennsylvania State University
Gilat, A., Mr.	Israel Ministry of Defense
Guard, H. E., Dr.	Office of Naval Research

Guenther, K., Dr.	University of Alabama
Haller, Wolfgang, Dr.	National Bureau of Standards
Inglehart, L., Dr.	Johns Hopkins University
Kelly, R., Dr.	Johns Hopkins University
King, R., Dr.	Department of Energy
Kuchinski, M.	Rutgers University
Laor, Uri Dr.	Nuclear Research Center, Israel
Lathabai, S.	Lehigh University
Legal LeSalle, E., Mr.	ESPCI, France
Lim, Dae-Soon	University of Illinois
Matthias, C., Ms.	University of Maryland
McMurdie, H.	The American Ceramic Society
Miller, P.J., Mr.	Naval Surface Weapons Center
Mizuhara, Kazuyuki	Japan Ministry of International Trade/Industry
Mysen, J., Dr.	Carnegie Institute
Neifeld, R., Dr.	Harry Diamond Labs
Nguyen, Christie, Ms.	University of Pennsylvania
Palamides, T., Mr.	Drexel University
Parker, H.	National Bureau of Standards
Ritter, A.P., Mr.	Martin Marietta Laboratory
Rosenblatt, D., Mr.	University of Pennsylvania
Sakai, C., Mr.	University of Maryland
Su, W., Mr.	Johns Hopkins University
Sun, Y., Mr.	Lanzhou Institute of Physics
Swanson, Peter L., Dr.	University of Colorado
Tewary, V.K., Prof.	Ohio State University
Thayer, J., Dr.	University of Cincinnati

Tierney, E., Ms.	University of Maryland
Trout, T., Mr.	University of Maryland
Vandiver, P.B., Dr.	Smithsonian Labs
Wang, Fu-Xing	Tsinghua University
Wang, Yusha	Tsinghua University
Whitler, J.	University of Maryland
Wilson, Annie, Ms.	Oberlin University
Winzer, S.R., Dr.	Martin Marietta Laboratory
Wong-Ng., W., Dr.	University of Maryland
Yeheskel, Ori, Dr.	Nuclear Research Center, Israel
Yellets, Jeffrey P.	The Pennsylvania State University
Ying, Tsi-Ning	Tsinghua University
Ying, X., Mr.	Fudan University, Shanghai, Peoples Republic of China
Zelibor, J., Dr.	University of Maryland
Zheng, Pei-Yi	RIPP

OUTPUTS AND INTERACTIONS

Ceramic Powder Characterization

Dragoo, A. L.; Hsu, S. M. Ceramic powder characterization - future needs. Proceedings of the International Workshop for Advanced Material Technology - Ceramics II, Nagoya, Japan, March 1987; to be published.

Wong-Ng, W.; Cook, L. P. X-ray studies of helium-quenched $Ba_2YCu_3O_{7-x}$. Adv. Ceram. Mater. 2(3B): 624-31; 1987.

Wong-Ng, W.; McMurdie, H. F.; Paretzkin, B.; Zhang, Y.; Davies, K. L.; Hubbard, C. R.; Dragoo, A. L.; Stewart, J. M. Standard x-ray diffraction powder patterns of sixteen ceramic phases. Powder Diffraction. 2(2): 106-117; 1987.

Wong-Ng, W.; Roth, R. S. X-ray characterization of 2BaO:CuO. J. Am. Ceram. Soc. Commun. in press.

Processing Science Group

Blendell, J.E.; Chiang, C.K.; Cranmer, D.C.; Freiman, S.W.; Fuller, E.R. Jr.; Drescher-Krasicka, E.; Johnson, W.L.; Ledbetter, H.M.; Bennett, L.H.; Swartzendruber, L.J.; Marinenko, R.B.; Myklebust, R.L.; Bright, D.S.; Newbury, D.E. Processing-property relations for $Ba_2YCu_3O_{7-x}$ high T_c superconductors. Adv. Ceram. Mat. 2(3B): 512-529; 1987.

Chiang, C.K.; Cook, L.P.; Chang, S.S.; Blendell, J.E.; Roth, R.S. Low temperature thermal processing of $Ba_2YCu_3O_{7-x}$ superconducting ceramics. Adv. Ceram. Mat. 2(3B): 530-538; 1987.

Coyle, T.W.; Ingel, R.P.; Willging, P.A. The temperature dependence of fracture toughness and yield strength in unstabilized zirconia crystals. Advanced Structural Ceramics, MRS Symposia Proceedings Series, 78: edited by P. F. Becher, M. V. Swain, and S. Sōmiya, Materials Research Society, Pittsburgh, PA; 89-86; 1987.

Coyle, T.W.; Palamides, T.R.; Freiman, S.W.; Fuller, E.R. Jr., Deshmukh, U. Crack-fiber interactions in ceramic matrix composites. Proceedings of Conference on "High Temperature Structural Composites: Synthesis, Characterization and Properties", The Metallurgical Society 1987 Regional Meeting, 1987, in press.

da Jornada, J.A.H.; Piermarini, G.J.; Block, S. Metastable retention of a high pressure phase of zirconia. J. Am. Ceram. Soc. 70: 1987.

Davis, K.; Roth, R.S.; Piermarini, G.J.; Block, S. Synthesis of and high pressure phase transition in single crystals of leucite ($KA\ell Si_2O_6$, and $RbA\ell Si_2O_6$, and $CsA\ell Si_2O_6$). Amer. Mineral., in press.

Ostertag, C.P. Technique for measuring stresses which occur during sintering of a fiber-reinforced ceramic composite. Am. Ceram. Soc., in press.

Tewary, V.K.; Fuller, E.R., Jr.; Thomson, R.M. Green function method for calculation of atomistic structure of grain boundary interfaces in ionic crystals," in Ceramic Microstructures 86: Role of Interfaces, 1986, in press.

Vaudin, M.D.; Handwerker, C.A.; Blendell, J.E. Electron microscopy studies of diffusion-induced grain-boundary migration in ceramics. J. de Physique, in press.

Ceramics Chemistry and Bioprocesses Group

Bellama, J. M.; Jewett, K. L.; Nies, J. D. Rates of methylation of mercury II species in water by organotin and organo silicon compounds. Environmental inorganic chemistry, A. F. Martell and K. J. Irgolic, eds., in press.

Manders, W. F.; Bellama, J. M.; Johannesen, R. B.; Parks, E. J.; Brinckman, F. E. Characterization of organometallic polymers by ^{13}C and ^{119}Sn NMR configurational/compositional triads in poly(tri-n-butyltin methacrylate/methyl metacrylate). J. Poly. Sci.; in press.

Olson, G. J.; Brinckman, F. E. Microbial metal leaching and resource recovery processes. In: Frontiers in bioprocessing, S. K. Sikdar, ed., CRC Press, Inc., Boca Raton, FL.; in press.

Olson, G. J.; Kelly, R. M. Microbiological processing of coal. In: Bioprocessing of fossil fuels, D. Wise, ed., CRC Press, Boca Raton, FL.; in press.

Parks, E. J.; Kool, L. B.; Brinckman, F. E. Characterization of organolead polymers in trace amounts by element-specific size exclusion chromatography. J. Chromatogr.; 370: 206-209; 1986.

Ritter, J. J.; Frase, K. A. Low temperature synthesis of ceramic powders for structural and electronic applications. In: Science of Ceramic Chemical Processing, L. L. Hench, D. R. Ulrich, eds., J. Wiley & Sons, New York; 497; 1986.

Ritter, J. J.; Roth, R. S.; Blendell, J. E. Alkoxide precursor synthesis and characteization of phases in the barium-titanium oxide system. J. Amer. Cer. Soc.; 69: 155; 1986.

Roth, R. S.; Ritter, J. J.; Parker, H. S.; Minor, D. B. Synthesis, stability and crystal chemistry of dibarium pentatitanate. J. Amer. Cer. Soc.; 69: 858; 1986.

Yeh, T. Y.; Godshalk, J. R.; Kelly, R. M.; Olson, G. J. Use of epifluorescence microscopy for characterizing the activity of Thiobacillus ferrooxidans on metal sulfides. Biotechnol. Bioengin.; in press.

High Temperature Chemistry

Bonnell, D. W.; Hastie, J. W.; and Zmbov, K. F. Transpiration mass spectrometry of liquid LiF -- vaporization thermochemistry and electron impact fragmentation. High Temp. High Press; in press 1987.

Cook, L. P.; Bonnell, D. W.; Hastie, J. W. Model for molten salt corrosion of (Co,Cr)-based superalloys NBSIR 87-3628 1987.

Cook, L. P.; Chiang, C. K.; Wong-Ng W.; Blendell, J. Thermal analysis of $Ba_2YCu_3O_{7-x}$ at 700-1000°C in air: Adv. Ceramic Materials 2(3B): 656-661; 1987.

Davidson, P. M. Phase separation in quadrilateral pyroxenes and olivines. Advances in Physical Geochemistry, S. Ghose, ed.; in press, 1987.

Davidson, P. M.; Burton, B. P. Order-disorder in omphacitic pryoxenes: A model for coupled substitutions in the point approximation. American Mineralogist, 72: 337-344; 1987.

Hastie, J. W.; Bonnell, D. W.; Schenck, P. K. Thermochemistry of materials by laser vaporization mass spectrometry, Part II. graphite. High Temp. High Press; in press (1987). See also NBSIR - 873561.

Hastie, J. W.; Bonnell, D. W.; Schenck, P. K. Laser induced vaporization mass spectrometry of refractory materials. Part I. Apparatus and the BN system. High Temp. Science; in press 1987.

Schenck, P. K.; Dennis, J.R. Graphics program for binary and ternary ceramic phase diagrams. In Proc. Users Conference on "User Applications of Alloy Phase Diagrams", Oct. 1986 Orlando, FL (Ed. L. Kauffman)

Schneider, S. J.; Hastie, J. W.; Holbrook, W. D. Phase diagrams for high tech. ceramics. In Elsevier pub. Proceedings of World Congress on High Tech. Ceramics, Milan, June (1986); in press 1987.

Synchrotron Radiation Group

Bennett, L. H.; Long, G. G.; Kuriyama, M.; Goldman, A. I. Local atomic structure in transition metal/metaloid glasses: Ni-Pin structure and bonding in noncrystalline solids. ed. by G. E. Walrafen and A. K. Revez., Plenum, NY 385-409; 1986.

Kennedy, J. J.; Amirtharaj, P.M.; Boyd, P.R.; Qadri, S.B.; Dobbyn, R. C.; Long, G. G. Growth and characterization of CdZnTe and HgZnTe. J. Cryst. Growth, in press.

Kuriyama, M.; Dobbyn, R. C.; Takagi, S.; Chow, L. C. Microradiography with an x-ray image magnifier. (translated in Japanese) (Invited article) SEIBUTSU-BUTSURI (Biophysics) 27: 1987.

Kuriyama, M.; Dobbyn, R. C.; Takagi, S.; Chow, L. C. Microradiography with an x-ray image magnifier: application to dental hard tissue. Medical Physics, in press.

Pella, P. A.; Dobbyn, R. C. Monochromatic synchrotron x-radiation for the EDXRF analysis of selenium in serum using total reflection geometry. Analytical Chemistry, in press.

Pella, P. A.; Dobbyn, R. C. Total reflection XRF analysis with monochromatic synchrotron radiation: advances in x-ray analysis. 31: Plenum, NY, in press.

Robbyn, R. C.; Kuriyama, M.; Takagi, S.; Chow, L. C. High resolution radiography: applications to biomedical imaging in biomedical engineering VI: recent development. eds. R. C. Eberhart and L. Howard McGregor and Werner Pub., in press.

Steiner, B.; Laor, U.; Kuriyama, M.; Long, G.G.; Dobbyn, R. C. Diffraction imaging of high quality bismuth silicon oxide with monochromatic synchrotron radiation: Implications for Crystal Growth. J. Crystal Growth, in press.

Glass and Composites

Baker, T. C.; Freiman, S. W. Fracture behavior of ceramics use in multilayer ceramics. Electronic Packaging Materials Science II, Materials Research Society, 72: 81; 1986.

Blendell, J. E. et al. Processing-property relations for $Ba_2YCu_5O_{7-x}$ high Tc superconductors. Advanced Ceramic Materials 2(3B): 530; 1987.

Chiang, C. K. et al. Low temperature thermal processing of $Ba_2YCu_3O_{7-x}$ AcerS superconducting ceramics. Advanced Ceramic Materials 2(3B): 530; 1987.

Freiman, S. W. Mechanical behavior of ferroelectric ceramics. Proceedings of the 6th IEEE Int. Symp. on Appl. of Ferroelectrics 367; 1986.

Freiman, S. W.; Michalske, T. A.; Bunker, B. C. Stress corrosion of ionic and mixed ionic/covalent solids. J. Am. Ceram. Soc. 69: 721; 1986.

White, G. S.; Freiman, S. W.; Wiederhorn, S.M.; Coyle, T. D. Effects of counter ions on crack growth in vitreous silica. To be published in J. Am. Ceram. Soc.

White, G. S.; Fuller, E. R., Jr.; Thomson, R. M. Environmentally enhanced crack growth in glass modeled by Greens function. Proc. of the TMS-AIME Fall Meeting, 1986.

Mechanical Properties Group

Chuang, T.-J.; Wiederhorn, S.M.; Chen, C.F. Transient behavior of structural ceramics under flexural creep. Creep and Fracture of Eng. Mater. and Struct. Ed. by B. Wilshire and R.W. Evans, Institute of Metals, 957-973; 1987.

Clarke, D.B.; Lawn, B.R.; Roach, D.H. The role of surface forces in fracture. Fracture Mechanics of Ceramics, R.C. Bradt, A.G. Evans, D.P.H. Hasselman and F.F. Lange, eds., Plenum, New York (8): 341; 1986.

Swanson, P/L.; Fairbanks, C.J.; Lawn, B.R.; Mai, Y.-W.; Hockey, B.J. Crack-interface grain bridging as a fracture resistance mechanism in ceramics: I. experimental study on alumina. J. Am Ceram. Soc. (70): 279; 1987.

Wiederhorn, S.M; Fuller, E.R. Jr. Design criteria for high temperature structural applications. Ceramic Materials and Components for Engines, W. Bunk and H. Hausner, eds. Deutsche Keramische Gesellschaft e.v., D-5340, Bad Honnef; 911-929; 1986.

Wiederhorn, S.M.; Chuck, L.; Chuang, T.-J.; Jakus, K. Standard tensile test development. Proceedings of the 24th Automotive Technology Development Contractors Coordinating Meeting, October 29, 1986, Soc. Automotive Engineers, Warrendale, PA; 1987.

Tribology Group

Gates, R.S.; Yellets, J.P.; Deckman, D.E.; Hsu, S.M. Considerations in ceramic friction and wear measurements, presented at the ASTM meeting in Cincinnati, OH, May 1987 (to be published as ASTM SP).

Hsu, S.M.; Ku, C.S.; Pei, P.T. Oxidative degradation mechanisms of lubricants, ASTM SP 916, 27; 1986.

Neihof, R.A.; Ross, M.M.; Munro, R.G.; Hsu, L.S.; Ku, C.S. High temperature lubricants from biodeuterated materials produced by algae, div. of petroleum symposium preprints, ACS, 32, 865; 1987.

Pei, P.; Hsu, S.M. Preparative liquid chromatographies method for the characterization of minor constituents of lubricating base oils. J. Chrom. 9 (15): 3311-3345; 1986.

Weeks, S.; Lawson, R.; Pei, P.T.; Hsu, S.M. Chemiluminescence instrumentation for fuel and lubricant oxidation studies. To be published in STLE Trans.

Optical Materials Group

Farabaugh, E. N.; Sun, Y. N.; Sun, J.; Feldman, A; Chen, H. H. A study of thin film growth in the ZrO_2-SiO_2 system. Laser Induced Damage in Optical Materials (1986), Boulder, CO; in press.

Feldman, A.; Sun, Y. N.; and Farabaugh, E. N. Bonding structure of silicon oxide films; in press.

Feldman, A.; Fuller, E.; Bendow; B.; Levin, K. Photoelastic characteristic of fluorozirconate and transition-metal fluoride glasses. Proceedings of the 4th International Symposium on Halide Glasses, Monterey, CA, 1987; in press.

Frederikse, H.; Feldman, A. Thermal wave inspection of heat resistant ceramic coatings. Proceedings of Conf. on Non-Destructive Testing of High Performance Ceramics, Boston, MA, 1987; in press.

Sun, Y. N.; Feldman, A.; Farabaugh, E. N. X-Ray photoelectron spectroscopy of O 1s and Si 2p lines in films of SiO_x formed by e-beam evaporation; in press.

Computerized Data Activities Group

Beech, F.; Miraglia, S.; Santoro, A.; Roth, R.S. Neutron study of the crystal structure and vacancy distribution in the superconductor $Ba_2YCu_3O_{9-x}$. Phys. Rev. B, 35(16): 8778-8781; 1987.

Ondik, H.M; Messina, C.G. Creating a materials database builder and producing publications for ceramic phase diagrams. ASTM Special Publication, Proceedings of the 1^{st} International Symposium on Computerized Materials Property Data, Nov. 1987, in press.

Roth, R.S.; Davis, K.L.; Dennis, J.R. Phase equilibria and crystal chemistry in the system Ba-Y-Cu-O. Advanced Ceramic Materials, 2(3B): Special Supplementary Issue, 303-312; 1987.

Roth, R.S.; Dennis, J.R.; McMurdie, H.F. Phase Diagrams for Ceramists, Volume 6, editors, American Ceramic Society, 1987, in press.

Roth, R.S.; Ettlinger, L.D.; Parker, H.S. Phase equilibria and crystal chemistry in the ternary system $BaO-TiO_2-Nb_2O_5$. J. of Solid State Chem., 68:, 330-339; 1987.

Schenck, P.; Dennis, J. PC-access to ceramic phase diagrams. ASTM Special Publication, Proceedings of the 1^{st} International Symposium on Computerized Materials Property Data, Nov. 1987, in press.

Wong-Ng, W.; Roth, R.S.; Swartzendruber, L.J.; Bennett, L.H.; Chiang, C.K.; Beech, F.; Hubbard, C.R. X-ray powder characterization of $Ba_2YCu_3O_{7-x}$. Advanced Ceramic Materials, 2(3B): Special Supplementary Issue, 565-576; 1987.

SELECTED TECHNICAL/PROFESSIONAL COMMITTEE LEADERSHIP

American Ceramic Society
    Glass Division
        S. W. Freiman
        Committee on Glass Standards Classification and Nomenclature
            M. J. Cellarosi, Chairman
        Editorial Committee
            S. Wiederhorn, Subchairman
    Basic Science Division
        Editorial Committee
            B. R. Lawn, Chairman
        Program Committee
            E. R. Fuller, Jr., Chairman
    Communication of the American Ceramic Society
            E. R. Fuller, Jr., Contributing Editor

American National Standards Institute (ANSI)
    Committee 43.1--Safety Standards for x-ray Diffraction and Fluorescence Analysis Equipment
        S. Block, Chairman

American Physical Society Editorial Board
    Review of Scientific Instruments
            P. K. Schenck

ASM International
    Energy Division Fuel Manufacturing Subcommittee
        S. J. Dapkunas, Chairman
    Journal of Engineering Materials
        S. J. Dapkunas, Associate Editor

American Society for Testing and Materials
    C14: Glass and Glass Products
            M. J. Cellarosi, Chairman
        C14.01: Nomenclature of Glass and Glass Products
                M. J. Cellarosi, Chairman
    F1: Electronics
        F1:02: Laser
                A. Feldman, Subcommittee Editor
        D2: Petroleum Products and Lubricants
            D2.09G: Oxidation
                    J. M. Perez, Chairman
                    C. S. Ku, Secretary
            E29.01: Advanced Ceramics, Organizational Meeting
                    M. J. Cellarosi
            E48.03.07: Bioleaching of Ores
                        G. J. Olson, Task Group Chairman
            E49.01.02 Computerization of Materials Property Data
                        C. R. Hubbard, Chairman

American Society of Mechanical Engineers
Research Committee on Tribology
S. Jahanmir, Chairman
Tribology Textbook Editorial Committee
S. Jahanmir, Chairman

COMAT Subcommittee on Structural Ceramics
S. M. Hsu, Member
COMAT Subcommittee on Superconductivity
S. J. Dapkunas, Member

Department of Energy
ECUT - Tribology Program, Guidance and Evaluation Panel
S. Jahanmir, Member
Materials Review Board for Nuclear Waste
H. P. R. Frederikse, Member

Gordon Research Conference on Tribology
S. M. Hsu, Chairman

International Commission for Optics
U. S. National Committee
B. Steiner, Chairman

International Energy Agency
Task II - International Standards
Assignment II-0-2 Powder Characterization Working Group
A. L. Dragoo, Member
Assignment II-0-3 Ceramic Characterization
E. R. Fuller, Jr., Member

International Union of Crystallography (IUCr)
Commission on Crystallographic Studies at Controlled Pressures and Temperatures
G. J. Piermarini, Chairman

International Union of Pure and Applied Chemistry
Commission II-3: High Temperature and Solid State Chemistry
J. W. Hastie, U.S.A. Associate Member

JCPDS-International Centre for Diffraction Data
C. R. Hubbard, Vice-Chairman

NAS Assessment Committee on Ceramic Tribology
S. M. Hsu, Member

National Academy of Sciences/National Research Council
Solid State Sciences Panel
H. P. R. Frederikse, Member

National Aeronautics and Space Administration
High Temperature Advisory Committee
D. W. Bonnell, Member

National Materials Advisory Board, National Academy of Sciences
- Committee on Ceramic Tribology
  - S. M. Hsu, Member
  - S. Jahanmir, Member

Oak Ride National Laboratory
- High Temperature Materials Laboratory Advisory Committee
  - S. M. Wiederhorn, Chairman

Society of Automotive Engineers
- Task Group on Recommended Practices for the Measurement of Unregulated Diesel Emissions
  - J. M. Perez, Chairman

Society of Tribologists and Lubrication Engineers
- Annual Meeting Program Committee
  - S. M. Hsu, Chairman
- Board of Directors
  - S. M. Hsu, Director
- Ceramics Activity
  - S. Jahanmir, Paper Solicitation Chairman
- Tribomaterials Committee
  - S. Jahanmir, Chairman
- Wear Technical Committee
  - S. Jahanmir, Paper Solicitation Chairman

Superconductor Applications Association
- E. R. Fuller, Jr., Member of Advisory Board

Versailles Project on Advanced Materials and Standards (VAMAS)
- International Round-Robin in Ceramic Working Area
  - S. W. Freiman, Co-chairman
  - E. R. Fuller, Jr., Co-chairman

INDUSTRIAL AND ACADEMIC INTERACTIONS

The Ceramics Division actively participates with Industry, Academia and other Government Laboratories in research programs of mutual interest. The following examples are illustrations .

INDUSTRIAL

1. Cummins Engine Co.

   A simple bench test method to evaluate diesel engine oil performance was developed in cooperation with Cummins Engine Co. Validation of the method is being performed using samples from Detroit Diesel Allison Division, GMC and Caterpillar, Inc.

2. John Deere and Company

   A joint project between NBS and John Deere and Co. was conducted to analyze the wear of ceramic engine components. Deposits on the component surface were analyzed using FTIR spectroscopy, SEM, and gel permeation chromatography coupled with graphite furnace atomic absorption spectroscopy.

3. Accumetrix Corporation

   H. P. R. Frederikse is collaborating with Dr. David Greenspan of Accumetrix Corporation to study the thermal and adhesive properties of plasma sprayed ceramic films. The films are prepared at Accumetrix and their properties are measured by means of photothermal radiometry. The research is expected to result in means for monitoring the production quality of ceramic coatings.

4. BDM Corporation

   A. Feldman collaborated with B. Bendow of the BDM Corporation in the measurement of the piezo-optic coefficients of fluoro-zirconate and heavy metal flouride glasses. The glasses are being developed for use as low loss infrared fiber-optic materials.

5. AT&T Bell Laboratories

   Dr. R. Cava and Dr. R. Roth of the Ceramics Division have collaborated on phase equilibria and crystal chemistry in the Ba-Y-Cu-O system.

6. AVX Corporation

   S. W. Freiman, D. C. Cranmer and M. L. Balmer of the Glass and Composite Group are working closely with Dr. Bharat Rawal of AVX on a program to understand the mechanical properties of multilayer ceramic capacitors. AVX is preparing specimens of differing composition and properties. These are subsequently tested at NBS. AVX claims that development of new materials based on these test results has saved the

company a substantial amount of money because of fewer capacitors lost during processing.

7. VAMAS

The Tribology Group is participating in the international wear test standardization project. Results of the first round-robin study have been submitted and recommendations for improved procedures are being prepared. Dr. Stephen Freiman and Dr. Edwin Fuller are leading a study to develop a test procedure for determining the stress corrosion susceptibility of ceramics. Approximately 20 laboratories in 6 countries are participating in an interlaboratory test programs.

8. Dupont-Savannah River

Drs. Hastie and Bonnell are collaborating with D. Bickford (Dupont) on vaporization behavior under processing conditions for borosilicate nuclear waste glass. Dupont provides samples and plant data and NBS provides basic data and process mechanisms for use by plant engineers.

9. Inland Steel

Drs. Plante and Bonnell have been collaborating with Dr. H. Pielet of Inland on the thermochemistry of blast furnace and steel slags and inorganic inclusions in steel. Dr. Pielet provides slag samples and data from plant experience, Dr. Plante is providing thermochemical data from high temperature mass spectrometry, while Dr. Bonnell supplies database and model techniques.

10. NASA/Cal Tech Jet Propulsion Lab (Pasadena, CA)

Dr. David Bonnell is collaborating and consulting on design of levitation systems for space applications.

11. Sandia Livermore Combustion Research Facility

John Hastie participated in a review workshop of future planning for the facility with special responsibility for research needs at combustion/materials interfaces.

12. IUPAC Commission II-3 on High Temperature and Solid State Materials

Dr. John Hastie, together with the other international members, planned the 5th conference on High Temperature and Energy-Related Materials held in Rome (May 1987). The Sixth conference is scheduled to be held at NBS (1989) and will be chaired by John Hastie.

13. Center for the Development of Commercial Crystal Growth in Space at Clarkson University

The Synchrotron Radiation Group is a member of the Center and is Conducting collaboration research on the structure of materials as a function of growth parameters.

14. Advanced Composite Materials Corporation

E.R. Fuller, Jr. and R.F. Krause, Jr. of the Processing Science Group are interacting with Dr. James F. Rhodes of ACM on microstructural and structural characterization of silicon carbide whisker-reinforced alumina composites, correlating mechanical properties to microstructural properties and to processing conditions.

15. Raytheon Company

S. Block and G.J. Piermarini of the Processing Science Group are interacting with Dr. R. Gentilman of Raytheon and Dr. P.E.D. Morgan of Rockwell International Science Center on a U.S. Navy program to develop tougher, infrared-transmitting missile windows through the evaluation of test samples for potential transformation toughening agents.

16. Stauffer Chemical Company

J.E. Blendell, E.R. Fuller, Jr., and L.C. Stearns of the Processing Science Group are interacting with Dr. F.A. Via of Stauffer Chemical on the sintering of $YBa_2Cu_3O_{7-x}$ ceramic superconductors formed from chemical precursor routes.

17. Max Planck Institut, Stuttgart, Federal Republic of Germany

J.E. Blendell and M.D. Vaudin of the Processing Science Group and C.A. Handwerker of the Metallurgy Division have collaborated with Dr. Wolfgang Kaysser of MPI on the sintering of ceramics and on diffusion induced, grain-boundary migration in ceramics and metals.

18. Naval Research Laboratory

Cooperative research between Dr. R.P. Ingel of the Naval Research Laboratory and T.W. Coyle of the Processing Science Group is performed concerning studies of phase transformations and toughening mechanisms in ZrO_2 containing ceramics.

19. Oak Ridge National Laboratory

T.W. Coyle, E.R. Fuller, Jr. and R.F. Krause, Jr. of the Processing Science Group are interacting with Drs. T.M. Besmann, D.P. Stinton, A.J. Caputo, and R. Lowden of ORNL on the microstructural and structural characterization of ceramic matrix composites produced by chemical vapor infilitration, correlating mechanical properties to microstructural properties and to processing conditions.

20. American Iron and Steel Intitute

G. J. Olson of the Surface Chemistry and Bioprocesses Group is a member of the AISI - Federal Laboratory Task A subcommittee on scrap recycling. The Group is also examining upgrading of ores and concentrates via biological removal of phosphorus, silicon, and sulfur.

21. Electric Power Research Institute

EPRI is funding a joint project between members of the Ceramic Chemistry and Bioprocesses Group and The Johns Hopkins University investigating microbio-logical bioasays to determine coal sulfur speciation and biodesulfurization of coal by extremely thermophilic bacteria.

22. Idaho Mining Association

F. E. Brinckman and G. J. Olson of the Ceramics Chemistry and Bioprocesses Group are working with members of the IMA and the Idaho National Engineering Laboratory to develop novel processes for extraction and separation of precious metals.

23. St. Joe Minerals

Members of the Ceramics Chemistry and Bioprocesses Group are investigating the bioleaching of St. Joe smelter wastes high in strategic metal content as a possible means for cost-effective recovery.

24. Technical Research Associates, Inc. and the U.S. Air Force

G. J. Olson of the Ceramics Chemistry and Bioprocesses Group is consulting with TRA, Inc. and the U.S. Air Force to develop novel microbial processes for leaching and recovery of gallium from domestic sources.

25. Cleveland Cliffs Iron Co. and Michigan Tech

Promising data obtained under the Steel Research Program by members of the Ceramics Chemistry and Bioprocesses Group have encouraged CCI and Michigan Tech to propose to the State of Michigan the development of an industrial process for biological removal of phosphorus from iron ores. NBS would be a consulting collaborator in the project.

JOINT INDUSTRIES/UNIVERSITIES

1. Detroit Diesel Allison Division, General Motors and Pennsylvania State University

   High temperature vapor phase lubrication studies in progress at the Pennsylvania State University funded under our program have resulted in cooperative studies between Penn State and Detroit Diesel Allison Division, GMC. The technology will be used in low heat rejection engine research studies at DDAD.

2. Gas Research Institute and Penn State University

   The Division is participating with GRI and PSU on research addressing the mechanical and tribological properties of materials for gas fired applications.

UNIVERSITIES

1. University of Michigan

   Joint research with Professor T.Y. Tien on the creep and creep rupture behavior of SiAℓON composites at high temperature. These materials were manufactured at the University of Michigan and characterized both microstructurally and mechanically at NBS by C.F. Chen a graduate student from the University of Michigan. This work was conducted in collaboration with T.-J. Chuang, and S.M. Wiederhorn of the Mechanical Properties Group.

2. Lehigh University

   Joint research with Professor Martin P. Harmer on the effect of microstructure on the fracture resistance of ceramic materials. The materials under study will be manufactured at Lehigh University and will be characterized and tested at the National Bureau of Standards by Dr. S. J. Bennison a Guest Scientist from Lehigh University. This work is being conducted in collaboration with Dr. B. R. Lawn of the National Bureau of Standards.

3. Northwestern University

   Joint research involves lubrication modeling between NBS and Prof. Herbert Cheng. The research focuses on the microelastohydrodynamic theories under wearing conditions. This is the first attempt at combining surface chemistry with surface mechanics to create a predictive wear model. Tim Ovaert of the Northwestern University has participated in the development of high temperature wear testing facility.

4. Pennsylvania State University

   The Tribology Group has several joint research projects with the Department of Chemical Engineering and the materials Research Laboratory at PSU. The research projects include fundamental studies

on the vapor phase lubrication of ceramic materials at high temperature; microstructural effects in ceramic wear processes; high temperature friction and wear tribometer design; and ceramic wear modeling which seeks to establish a theoretical understanding of ceramic wear processes.

5. University of Illinois

   Steven Danyluk and Dae-Soon Lim of the Department of Civil Engineering, Mechanics, and Metallurgy are conducting joint research with NBS. The project centers on an investigation of the fundamental mechanisms of friction, wear, and surface damage in tribological applications of advanced ceramics.

6. University of Maryland

   S. Jahanmir of the Tribology Group is Adjunct Professor in the Department of Mechanical Engineering. He participates in joint research activities between NBS and the University of Maryland.

7. Tsinghua University

   J. Dong, X. Dong, F. Wang, Y. Wang and T. Ying of Tsinghua University are conducting tribology research at NBS. This joint research activity is concerned with the mechanisms of wear and lubrication of ceramics.

8. North Carolina State University

   A. Feldman and E. N. Farabaugh collaborated with R. Nemanich of North Carolina State University in measuring the Raman spectrum of a diamond film deposited at NBS.

9. University of Pennsylvania

   Prof. P. Davies and Dr. R. Roth are collaborating on the properties and structure of microwave dielectrics and high T_c superconductors.

10. North Carolina State University

    Dr. R. Porter and J. Dennis of the Ceramics Division are collaborating on wetting during melt formation of the 1:2:3 superconductor phase.

11. Penn State University

    Dr. John Hastie participated in the Ceramics Department graduate seminar program and Drs. John Hastie and Ernest Plante of NBS and Prof. C. Pantano (Penn State) are collaborating on studies of vaporization mechanisms of Ge-Se-Sb glass systems.

12. The Johns Hopkins University

Robert Kelly of the Chemical Engineering Department and G. J. Olson and F. E. Brinckman are conducting joint research on microbial processing of coal. Olson is guest lecturer in Chemical Engineering Department. Another project on characterizing microbial activity on mineral surfaces is being conducted with JHU and Martek Corp., Columbia, MD.

13. University of Cincinnati

Scientific collaboration with Professor John S. Thayer on molecular mechanisms of metal solubilization and transformation by biogenic metabolites is being pursued.

14. University of Maryland

Members of the Ceramics Chemistry and Bioprocesses Group are collaborating with Professor Michael Bellama and his doctoral students on biological and chemical transformations of organometallic materials in environmental situations. Brinkman is adjunct professor in the Chemistry Department.

15. University of New Hampshire

The Surface Chemistry and Bioprocesses Group is collaborating with Professor Richard H. Blakemore on in vivo characterization of metal particle formation rates and sites in magnetite-depositing bacteria, using SANS characterization. G. J. Olson, F. E. Brinckman and K. Rhyne are participating in the research.

16. University of Siena, Italy

G. J. Olson and F. E. Brinckman are collaborating with Dr. Franco Baldi on microbiological leaching of metal ores.

17. University of the District of Columbia

F. E. Brinckman is collaborating with Professor George Eng on molecular properties of organometallic compounds.

18. Georgia Tech Research Institute

T.W. Coyle and E.R. Fuller, Jr. of the Processing Science Group are interacting with Dr. Thomas Starr of GTRI on the microstructural and structural characterization of ceramic matrix composites correlating mechanical properties to microstructural properties and to processing conditions.

19. Federal University of the Rio Grande of the South (UFRGS)
Porto Alegre, Brazil

G.J. Piermarini of the Processing Science Group has initiated a collaborative research program with Prof. J. A. H. da Jornada at the UFRGS University on densification and sintering of ceramic materials using presses to achieve large-scale sample volumes for improved product testing and evaluation.

20. Harvard University, Division of Applied Sciences

S. Block and G.J. Piermarini of the Processing Science Group have consultated with Drs. M. Aziz and E. Nygren of Harvard University on setting up a high pressure lab with diamond anvil pressure cells for low-temperature use.

21. Howard University, Chemistry Department

S. Block and G.J. Piermarini of the Processing Science Group have collaborated with Prof. G. Walrafen of Howard University on the study of pressure effects on the structure of liquid and solid phases of water.

22. University of Bayreuth, Federal Republic of Germany

G.J. Piermarini of the Processing Science Group has consulted with Dr. H. Olijnyk of the Research Institute for Experimental Geochemistry and Goephysics, University of Bayreuth on establishing a high-pressure laboratory for X-ray diffraction and optical spectroscopy studies at ultra-high pressures with diamond anvil cells.

23. Drexel University

The Glass and Composite Group is conducting a joint program with Dr. M. J. Koezak of Drexel University on the fracture behavior of ceramic matrix composites.

STANDARD REFERENCE MATERIALS

The Division provided science, industries, and government a central source of well-characterized materials certified for chemical composition of physical or chemical properties. These materials are issued with a certificate and are used to calibrate instruments, to evaluate analytical methods, or to produce scientific data which can be referred to a common base.

DESCRIPTION	SRM NUMBER
Alumina Elasticity	718
Alumina Glass Anneal Point	714
Alumina Glass Anneal Point	715
Alumina Melting Point	742
Aluminum Magnetic Susceptibility	763-1
Aluminum Magnetic Susceptibility	763-2
Aluminum Magnetic Susceptibility	763-3
Barium Glass Anneal Point	713
Borosilicate Glass Composition	93(A)
Borosilicate Glass Thermal Expansion	731L1
Borosilicate Glass Thermal Expansion	731L2
Borosilicate Glass Thermal Expansion	731L3
Cadmium Vapor Pressure	746
Chlorine in Base Oil	1818
Container Glass Composition	621
Container Glass Leaching	622
Container Glass Leaching	623
Copper Thermal Expansion	736L1
Fused Silica Thermal Expansion	739L1
Fused Silica Thermal Expansion	739L2
Fused Silica Thermal Expansion	739L3
Glass Dielectric Constant	774
Glass Electrical Resist	624
Glass Fluorescence Source	477
Glass Liquidus Temperature	773
Glass Refractive Index	1820
Glass Sand (High Iron)	81A
Glass Sand (Low Iron)	165A
Glass Stress Optical Coefficient	708
Glass Stress Optical Coefficient	709
Gold Vapor Pressure	745
High Boron Glass Viscosity	717
Intensity XRD Set	674
Lead Barium Glass Composition	89
Lead Glass Anneal Point	712
Lead Glass Viscosity	711
Liquids Refractive Index	1823
Low Boron Glass Composition	92
Lube Oil Oxidation Test Kit	1817

Lube Oxidation Catalysts	8500
Lubricant Oxidation Research Test Kit	8500a
MNF_2 Magnetic Susceptibility	766-1
Mica X-Ray Diffraction	675
Neutral Glass Anneal Point	716
Nickel Magnetic Susceptibility	772
Opal Glass Composition	91
Palladium Magnetic Susceptibility	765-1
Palladium Magnetic Susceptibility	765-2
Palladium Magnetic Susceptibility	765-3
Platinum Magnetic Susceptibility	764-1
Platinum Magnetic Susceptibility	764-2
Platinum Magnetic Susceptibility	764-3
Refractive Index Glass	1822
Respirable Quartz	1878
Ruby EPR Absorption	2601
Sapphire Thermal Expansion	732
Silicon X-Ray Diffraction	640(b)
Silver Vapor Pressure	748
Soda Lime Flat Glass Composition	S620
Soda Lime Float Composition	1830
Soda Lime Glass Viscosity	710
Soda Lime Sheet Composition	1831
Sulfur in Base Oil	1819
Toluene 5 ML	211C
Tungsten Thermal Expansion	737

APPENDIX

CERAMICS DIVISION ORGANIZATION

Division Office Telephone Number: 301-975-6119

Division Chief: Stephen M. Hsu

Deputy Chief: S. J. Dapkunas

Administrative Officer: Sonja C. Lightbody

PROCESSING

Ceramic Powder Characterization
Alan Dragoo, 975-5785

Processing Science
Edwin Fuller, 975-5797

Ceramic Chemistry and Bioprocesses
Frederick Brinckman, 975-5737

STRUCTURE/STABILITY

High Temperature Chemistry
John Hastie, 975-5754

Synchrotron Radiation
Masao Kuriyama, 975-5974

Glass and Composites
Stephen Freiman, 975-5761

PROPERTIES AND PERFORMANCE

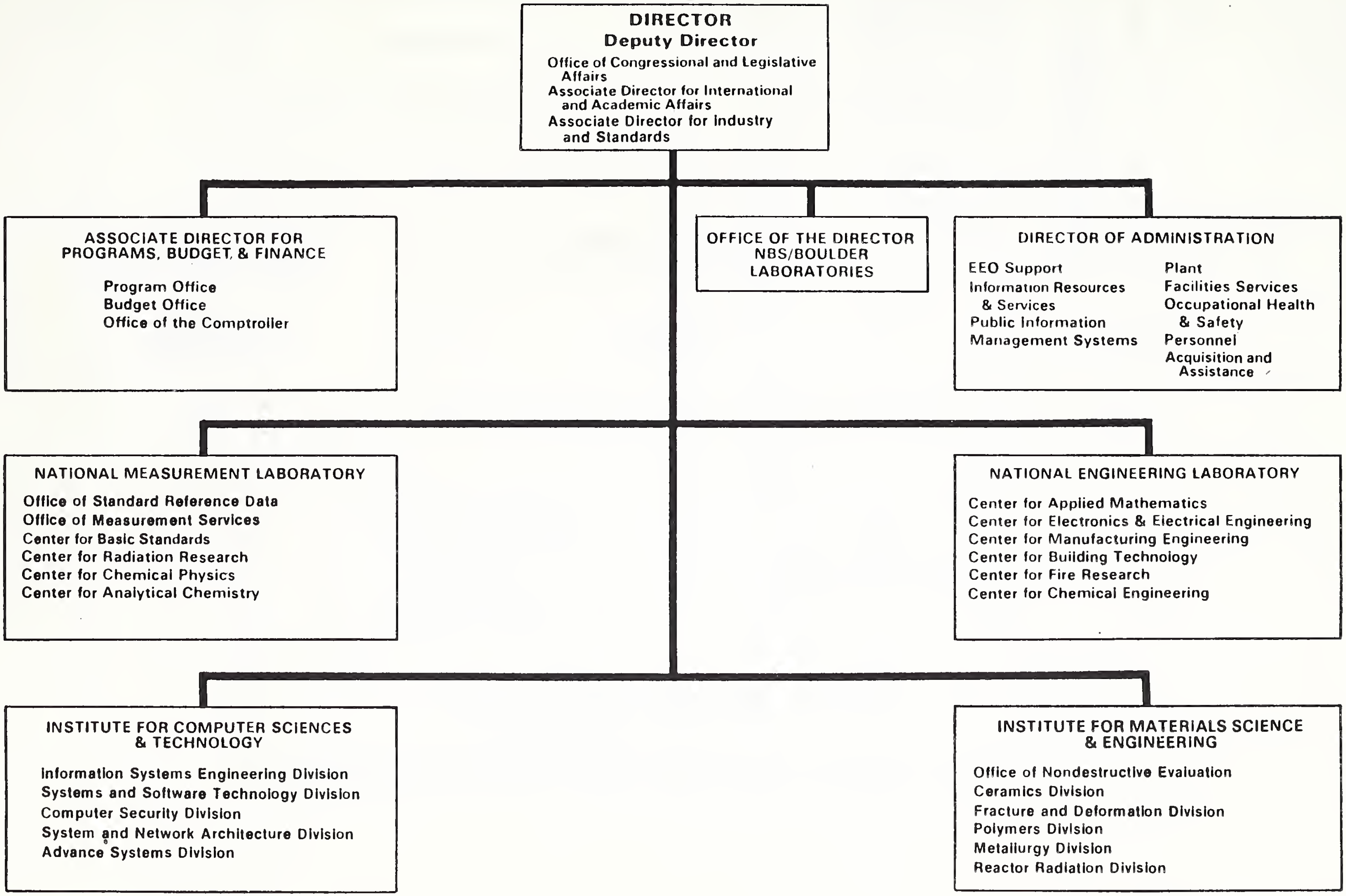
Mechanical Properties
Sheldon Wiederhorn, 975-5772

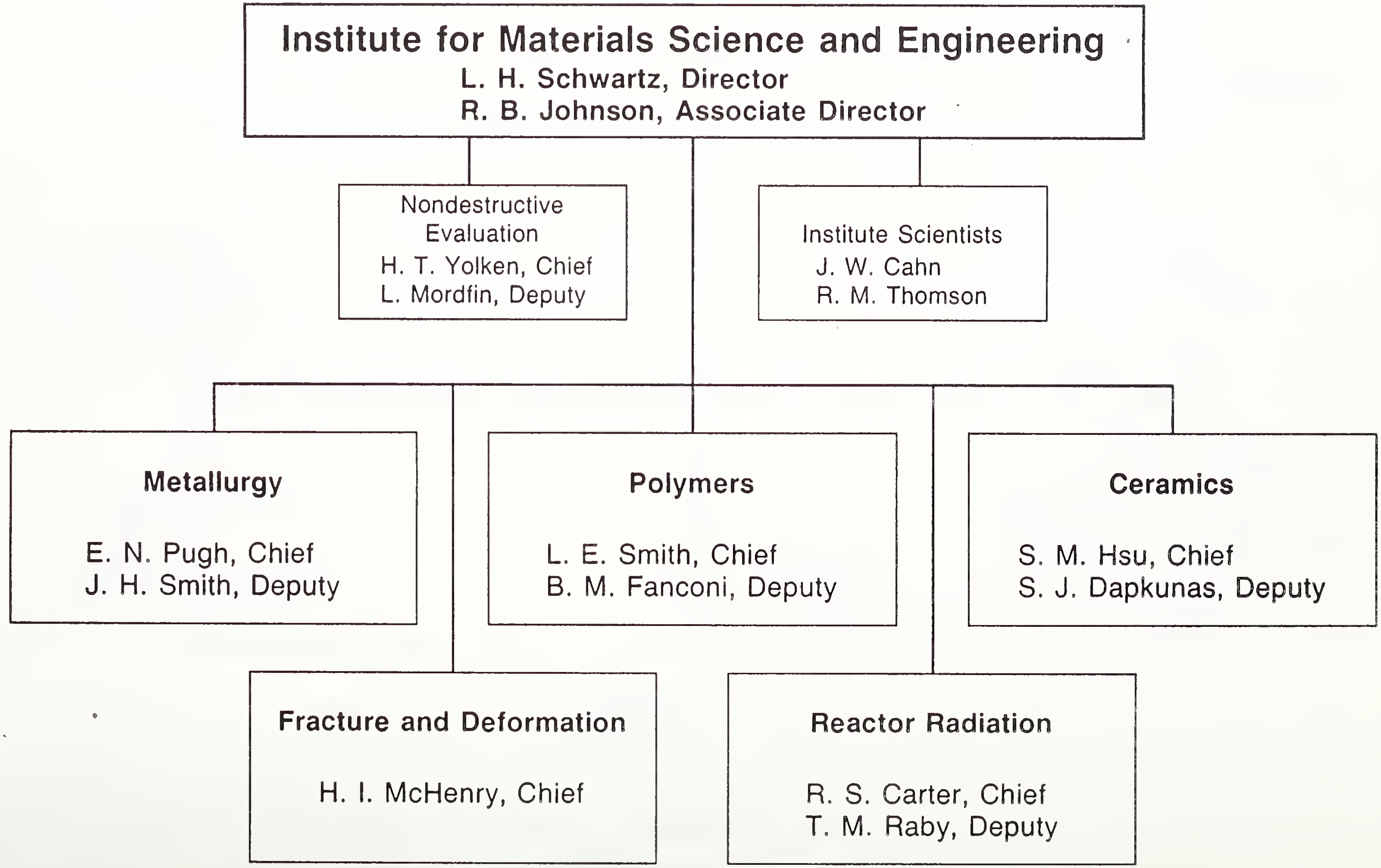
Tribology
Said Jahanmir, 975-3671

Optical Materials
Albert Feldman, 975-5740

Computerized Data Activities
Camden Hubbard, 975-6121

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards




Institute for Materials Science and Engineering
L. H. Schwartz, Director
R. B. Johnson, Associate Director
Nondestructive Evaluation
H. T. Yolken, Chief
L. Mordfin, Deputy
Institute Scientists
J. W. Cahn
R. M. Thomson
Metallurgy
E. N. Pugh, Chief
J. H. Smith, Deputy
Polymers
L. E. Smith, Chief
B. M. Fanconi, Deputy
Ceramics
S. M. Hsu, Chief
S. J. Dapkunas, Deputy
Fracture and Deformation
H. I. McHenry, Chief
Reactor Radiation
R. S. Carter, Chief
T. M. Raby, Deputy

FORM NBS-114A (REV. 11-84)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions)	1. PUBLICATION OR REPORT NO. 87-3612	2. Performing Organ. Report No.	3. Publication Date November 1987

4. TITLE AND SUBTITLE

Ceramics Division - Technical Activities 1987

5. AUTHOR(S)

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
U.S. DEPARTMENT OF COMMERCE
GAITHERSBURG, MD 20899

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

NBS - Ceramics Division 420
Building 223, Room A257
Gaithersburg, MD 20899

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Current programs of the Ceramics Division are reviewed.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Composites; glass; mechanical properties; optical materials; powder characterization; superconductivity; thermodynamics; tribology

13. AVAILABILITY

- X Unlimited
- ☐ For Official Distribution. Do Not Release to NTIS
- ☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.
- X Order From National Technical Information Service (NTIS), Springfield, VA 22161

14. NO. OF PRINTED PAGES

91

15. Price

$ 13.95

USCOMM-DC 85-6006